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INVESTIGATIONS ON THE SULPHONPHTHALEÏNS.[1]

V.—ON SULPHONPHTHALEÏN AND SOME RELATED COMPOUNDS.

BY JOHN WHITE, JR.

In order, if possible, to get further light on the nature of sulphonphthaleïn, I have undertaken at Professor Remsen's suggestion an investigation of some of its derivatives and of some related compounds. Great difficulties were encountered throughout the work, and the results are, therefore, not as satisfactory as could be desired. Still some facts of interest have been established, and a brief account of the work is herewith communicated.

Preparation of sulphonfluoresceïn from dioxybenzenesulphonic acid.—The method used was that described by Remsen and Linn.[2] The dioxybenzoylbenzenesulphonic acid was placed in a test-tube and heated in a sulphuric-acid bath. By means of a thermometer placed in the test-tube the temperature could be noted, and the mass could, at the same time, be stirred from time to time: a quite advantageous precaution, since, by frequent stirring, the reaction takes place much more rapidly. The temperature of the bath was allowed to rise gradually; at about 100°–110° the acid melts, the liquid thus formed being of a dark-red color; this rapidly becomes darker, and, when

[1] From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1891.

[2] This Journal, 11, 73.

the temperature is raised to 160°–170°, where the reaction takes place most readily, it becomes a deep brown; the mass meanwhile becomes quite viscous, and a considerable amount of water is given off. After heating for several hours the reaction is at an end. The mass was allowed to become cool, then was treated with cold water, and filtered. The sulphonfluoresceïn remaining on the filter was thoroughly washed with cold water to remove the orthosulphobenzoic acid formed as one of the products of the reaction:

$$2(OH)_2C_6H_3.CO.C_6H_4.SO_2OH =$$

$$C\begin{cases} C_6H_3 < \begin{matrix} OH \\ O \end{matrix} \\ C_6H_3 < OH \\ C_6H_4.SO_2 \\ O \text{——} \end{cases} + C_6H_4 < \begin{matrix} COOH \\ SO_2OH \end{matrix} + H_2O.$$

It was then dissolved in alkalies, a moderately concentrated solution of caustic potash being used for this purpose. This solution is intensely fluorescent, even when extremely dilute, and is of a pale yellow color in transmitted light. The alkaline solution, after filtration, was treated with dilute acid, when the sulphonfluoresceïn was precipitated as a reddish-brown flocculent precipitate; this was washed a few times by decantation, then on the filter with the aid of the pump.

Sulphonfluoresceïn is very difficultly soluble in hot alcohol and in hot glacial acetic acid. It is more easily soluble in hot than in cold water, though but slightly soluble in either. It dissolves with great ease in alkalies, forming the intensely fluorescent solutions spoken of above.

Action of bromine on sulphonfluoresceïn.—Von Baeyer[1] found that when fluoresceïn is treated with bromine, three substitution-products are obtained, according to the proportion of bromine used: monobromfluoresceïn, dibromfluoresceïn, and tetrabromfluoresceïn (eosin). He was unable to obtain the tribromfluoresceïn. Of these he only succeeded in isolating in pure condition the dibrom- and tetrabromfluoresceïns, and from the latter a number of well-defined salts were obtained.

In the case of sulphonfluoresceïn, the principal action of bromine is to form the *dibromsulphonfluoresceïn*, and probably

[1] Ann. Chem. (Liebig), **183**, 36.

a *monobromsulphonfluoresceïn*. The tribrom- and tetrabrom-substitution-products could not be obtained. Dry sulphonfluoresceïn was suspended in four or five times its weight of glacial acetic acid in a small beaker; to this was added a twenty-per cent. solution in glacial acetic acid, in the proportion of one molecule of bromine to one of sulphonfluoresceïn. Reaction immediately took place, the liquid becoming warm from the reaction, and fumes of hydrobromic acid being given off. A solid product was thus obtained, somewhat lighter in color than the original sulphonfluoresceïn. It was filtered off, washed with glacial acetic acid, in which it is much less soluble than in water, and placed in a desiccator containing solid caustic potash to remove the last traces of acetic acid. The bromine product is slightly soluble in alcohol and water. It is insoluble in ether, chloroform, glacial acetic acid, and petroleum-ether. In alkalies it dissolves readily, forming strongly fluorescent solutions, which show a very decided pink in transmitted light, very similar to that produced by eosin. Estimations of sulphur and bromine gave the following results:

I. 0.1195 gram substance gave 0.0550 gram $BaSO_4$ (Liebig).

II. 0.1596 gram substance gave 0.0782 gram AgBr (Carius).

	Calculated for $C_{19}H_{11}BrO_5S$.	Found.
S	7.17	6.32
Br	17.88	20.85

It was concluded from these results that some dibromsulphonfluoresceïn had been formed at the same time as the monobrom-product, and that a mixture of the two was thus obtained. It was then decided to prepare other bromine substitution-products of sulphonfluoresceïn to see if some of these could be obtained in pure condition.

With this in view, sulphonfluoresceïn was treated with two molecules of bromine in the manner described above. The action was in every respect similar to that described in the preceding experiment, except that in this case, after standing for a short time, the whole mass became almost solid, and the reaction appeared to take place more readily than in the previous case. The product obtained was much like that obtained in the first experiment, but appeared to be more gran-

ular, and was hence easier to wash. The following analyses were obtained:

I. 0.1187 gram substance gave 0.0526 gram $BaSO_4$ (Liebig).

II. 0.0772 gram substance gave 0.0509 gram AgBr (Carius).

III. 0.0903 gram substance gave 0.0600 gram AgBr (Carius).

IV. 0.29685 gram substance, heated for three hours at 160°, lost 0.00951 gram H_2O.

	Calculated for $C_{19}H_{10}Br_2O_4S+H_2O$.	Found. I.	II.	III.	IV.
S	5.89	6.09	....	....	....
Br	29.39	....	28.06	28.27	....
H_2O	3.30	....	....	....	3.20

The bromine in this product is somewhat lower than that required for dibromsulphonfluorescein, and further experiments in this line failed to give a pure dibromine product.

Three molecules of bromine were next added to one molecule of sulphonfluorescein. The action took place as in previous experiments. Estimations of sulphur and bromine gave the following results:

I. 0.1240 gram substance gave 0.0504 gram $BaSO_4$ (Liebig).

II. 0.0919 gram substance gave 0.0611 gram AgBr (Carius).

	Calculated for $C_{19}H_8Br_3O_4S$.	Calculated for $C_{19}H_{10}Br_3O_4S+H_2O$.	Found. I.	II.
S	5.30	5.89	5.59	....
Br	39.65	29.39	....	28.29

Another product was prepared by treating sulphon-fluorescein with four molecules of bromine. Reaction took place at once, with copious evolution of fumes of hydrobromic acid.

An analysis of the product gave the following figures:

I. 0.1810 gram substance gave 0.2883 gram CO_2 and 0.0476 gram H_2O.

II. 0.2768 gram substance gave 0.4293 gram CO_2 and 0.0733 gram H_2O.

III. 0.1325 gram substance gave 0.0533 gram $BaSO_4$ (Liebig).

IV. 0.2175 gram substance gave 0.0918 gram $BaSO_4$ (Liebig).

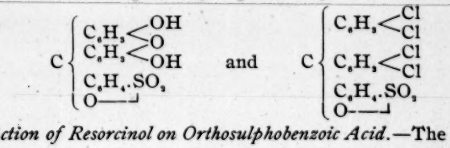
V. 0.0703 gram substance gave 0.0466 gram AgBr (Carius).

	Calculated for $C_{19}H_{12}Br_2O_8S+H_2O$.	Found. I.	II.	III.	IV.	V.
C	41.91	43.44	42.30	....	....	....
H	2.21	2.93	2.94	....	....	....
Br	29.39	....	....	....	....	28.21
S	5.89	....	....	5.52	5.76	....

It appears probable, from a consideration of the results obtained, that the principal product of the action of bromine on sulphonfluoresceïn is a *dibromsulphonfluoresceïn*, but that, owing to the difficulty attending the separation of the products formed in the reaction, it cannot be obtained in pure condition. The dibrom substitution-product may be mixed with one or more of the other bromine products, or perhaps the action is not complete, and this appears to be shown by the fact that the analyses for bromine, while agreeing very well for the various preparations, are too low in all cases; the carbon and hydrogen are likewise too high.

The action of *acetic anhydride* on dibromfluoresceïn gave a product insoluble in alkalies, and, therefore, probably an acetyl derivative. The analyses of this product did not, however, give figures agreeing with any probable formula.

Phosphorus pentachloride acts upon sulphonfluoresceïn readily at 125°–130°, giving rise to the formation of a product, with a bright red color, soluble to some extent in alcohol and in alkalies. The solution in alkalies first assumes a deep cyanide-blue color which, upon standing, soon changes to green, then to pale yellow, and finally becomes colorless. The analyses gave figures which showed that the substance was an impure tetrachlorine product, the relation of which to the fluoresceïn is probably expressed by these formulas:



Action of Resorcinol on Orthosulphobenzoic Acid.—The preparation of sulphonfluoresceïn by heating dioxybenzoylbenzenesulphonic acid involves a splitting off of orthosulphobenzoic acid (see equation, p. 546). It was thought that, by mixing the dioxy acid with resorcinol a larger yield of sulphonfluor-

escein might be obtained. It was found, however, that at least two products were formed, one of which was sulphonfluorescein, the other or others resulting in all probability from the action of the resorcinol on the orthosulphobenzoic acid. Hence, experiments were made on the action of these two substances upon each other. Fahlberg and Barge,[1] describe some experiments performed by them on the action of resorcinol on orthosulphobenzoic acid. They found that when orthosulphobenzoic acid is heated with either 2 or 4 molecules of resorcinol, a condensation-product is obtained containing four resorcinol residues. They ascribe to it the formula $C_{31}H_{20}O_8S+4H_2O$, and give the following analyses:

	Calculated for $C_{31}H_{20}O_8S+4H_2O$.	Found. I.	II.	III.	IV.
C	59.60	59.12	59.04	59.68	....
H	4.50	....	4.97	4.91	....
S	5.13	5.24	5.05	5.38	5.34
H_2O	11.54	11.42	....	11.20	11.38

As there were very few or no details given and no further investigation made, it seemed desirable, especially since it is in line with the series of investigations which have been carried on in this laboratory for some years past, to repeat the work of Fahlberg and Barge, and also to see if other phenol residues might be introduced in the same way.

I.—Orthosulphobenzoic acid and resorcinol (1:4) were heated together in a sulphuric-acid bath. The temperature was allowed to rise gradually; at 100°–110° the mixture melted to a deep-red liquid, which gradually grew darker as the temperature rose. At 140° reaction took place, bubbles were seen to pass up through the liquid, water was given off, and in the course of a few hours the mass became quite viscous and dark in color. The product thus obtained was, when cold, hard, quite brittle, and of a reddish-brown color, somewhat different from that of sulphonfluorescein. The physical properties of the substance are worthy of comment. When rubbed it shows electrical phenomena; when treated with water in the cold it softens to a slight extent, then becomes hard again, the process being similar to the setting of plaster of Paris or of cement; this is even more noticeable if it is

[1] Ber. d. chem. Ges., **22**, 765.

heated with water. At the boiling-point of water it is a soft, dark-green mass, of the consistency of tar, and floats on the surface of the water. Upon cooling the mass becomes hard and brittle and sinks in the water. When the mass is heated in an air-bath to a temperature of 120° the same phenomenon is noticed. This change in physical condition does not appear to be attended by any change in chemical composition. The substance dissolves quite readily in alkali, forming an intensely fluorescent solution, but the fluorescence is of a different character from that of sulphonfluoresceïn. The solution is of a deep-red color in concentrated form, showing a delicate pink in dilute form, while, as before stated, sulphonfluoresceïn shows a yellow color in dilute solution.

It is precipitated from the alkaline solution by acids, and for purposes of purification this method was used. The precipitate is flaky, and very difficult to wash thoroughly. After purification it was carefully examined. It is easily soluble in alcohol and ether, insoluble in chloroform, water, petroleum-ether, and in cold glacial acetic acid, slightly soluble in warm. Analysis gave the following results :

I. 0.2231 gram substance gave 0.5281 gram CO_2 and 0.0990 gram H_2O.

II. 0.1703 gram substance gave 0.0428 gram $BaSO_4$ (Liebig).

III. 1.2564 grams substance, heated for four hours at 140°, lost 0.0788 gram H_2O.

IV. 0.6253 gram substance, heated for five hours at 140°, lost 0.0404 gram H_2O.

V. 0.1712 gram substance gave 0.4054 gram CO_2 and 0.0706 gram H_2O.

VI. 0.7668 gram substance, heated for four hours at 140°, lost 0.0384 gram H_2O.

VII. 0.2790 gram substance, heated for five hours at 140°, lost 0.0156 gram H_2O.

	Calculated for $C_{21}H_{20}O_6S + 4H_2O$. (Fahlberg and Barge.)	Calculated for $C_{42}H_{38}O_{13}S + 3\frac{1}{2}H_2O$.
C	59.60	64.57
H	4.50	4.39
S	5.13	4.01
H_2O	11.54	7.88

	Found.						
	I.	II.	III.	IV.	V.	VI.	VII.
C	64.56	...	...	...	64.59	...	...
H	4.93	...	...	...	4.58	...	...
S	....	3.45	...	...	....	...	...
H_2O	....	...	6.27	6.46	....	5.01	5.59

Four other sulphur-estimations gave respectively 4.26, 3.97, 4.11, and 4.24 per cent.

The results of all my analyses point to the conclusion that orthosulphobenzoic acid and resorcinol react under the conditions above described to form a product containing six residues of resorcinol united to one of the acid. Accordingly experiments were next made in which the substances were mixed in the proportion of 1 molecule of the acid to 6 of resorcinol. The analyses of the products gave the following results:

Preparation I.

I. 0.2176 gram substance gave 0.5177 gram CO_2 and 0.0944 gram H_2O.

II. 0.1345 gram substance gave 0.0362 gram $BaSO_4$ (Liebig).

III. 1.3625 grams substance, heated for four hours at 140°, lost 0.0820 gram H_2O.

Preparation II.

I. 0.2655 gram substance gave 0.0752 gram H_2O (combustion).

II. 0.1744 gram substance gave 0.0436 gram $BaSO_4$ (Liebig).

III. 1.2358 grams substance, heated for four hours at 140°, lost 0.0675 gram H_2O.

Preparation III.

0.2559 gram substance gave 0.6115 gram CO_2 and 0.1153 gram H_2O.

	Calculated for $C_{43}H_{32}O_{16}S+3\frac{1}{2}H_2O$.	Found. Prep. I.			Prep. II.			Prep. III.
		I.	II.	III.	I.	II.	III.	
C	64.57	64.93	...	...	...	...	...	65.17
H	4.39	4.82	...	...	4.98	...	...	5.01
S	4.01	...	3.70	...	...	3.44	...	...
H_2O	7.88	...	...	6.02	...	...	5.46	...

It will be observed that in all cases the estimations of water of crystallization are low. An explanation of this will be offered later.

The results obtained do not agree as well as could be wished, but, considering the nature of the substance and the difficulty attending its purification, this is not surprising.

Since it was difficult to decide between several formulas—some containing six resorcinol residues, with varying amounts of water of crystallization; others containing four resorcinol residues, but which contain much less water than that ascribed to it by Fahlberg and Barge—it seemed desirable to analyze the dehydrated substance, as the differences between the tetra- and hexaresorcinol derivatives are more marked. After heating for several hours at 140°, the residues were analyzed:

Product I_4[1].

I. 0.1188 gram substance gave 0.2966 gram CO_2 and 0.0587 gram H_2O.

II. 0.1320 gram substance gave 0.3317 gram CO_2 and 0.0569 gram H_2O.

III. 0.1130 gram substance gave 0.0285 gram $BaSO_4$ (Liebig).

IV. 0.1374 gram substance gave 0.0364 gram $BaSO_4$ (Liebig).

Product II_4.

I. 0.1393 gram substance gave 0.3462 gram CO_2 and 0.0542 gram H_2O.

II. 0.1018 gram substance gave 0.0302 gram $BaSO_4$ (Liebig).

III. 0.1258 gram substance gave 0.0398 gram $BaSO_4$ (Liebig).

Product III_6.

I. 0.1224 gram substance gave 0.3078 gram CO_2 and 0.0439 gram H_2O.

II. 0.1208 gram substance gave 0.0289 gram $BaSO_4$ (Liebig).

Product IV_6.

I. 0.1379 gram substance gave 0.3459 gram CO_2 and 0.0566 gram H_2O.

[1] The small figures 4 and 6 refer to the preparations made by using 4 and 6 molecules respectively of resorcinol.

II. 0.1195 gram substance gave 0.0283 gram $BaSO_4$ (Liebig).

III. 0.1492 gram substance gave 0.0353 gram $BaSO_4$ (Liebig).

On comparing these results with those calculated for substances containing 4 and 6 residues of resorcinol, the following table will show that they are more in accord with those required by a substance containing 6 such residues:

	Calculated for $C_{31}H_{26}O_8S$ (4 Resorcin).	Calculated for $C_{43}H_{36}O_{10}S+H_2O$ (6 Resorcin).	Found. Prep. I_4.		Prep. II_4.		Prep. III_4.	Prep. IV_4.	
			I.	II.	I.	II.		I.	II.
C	67.38	68.41	68.10	68.62	67.78	...	68.58	68.41	...
H	3.63	3.98	5.49	4.79	4.33	...	3.99	4.56	...
S	5.80	4.25	3.47	3.64	4.08	4.34	3.29	3.26	3.25

It appears from this that all the water of crystallization is not driven off at 140°, but that there still remains 1 molecule. This explains the low results in the previous determinations of water, for it will be seen from a study of those results that the difference between the percentages found and the calculated is just about what is required for 1 molecule of water. An attempt was made to drive off this last molecule of water. The temperature of the air-bath was allowed to rise gradually above 140°, and weighings made from time to time showed a gradual loss in weight. When a temperature of 180° was reached a surprising observation was made. On removing the weighing-tube containing the substance from the bath, a strong odor of sulphuretted hydrogen was noticed. A test was made with silver nitrate and with lead acetate solutions, and both gave the characteristic reactions for hydrogen sulphide. This was an entirely unaccountable decomposition, and one for which no explanation can be offered.

Taking all the facts into consideration, it appears that the subject is an extremely difficult one to deal with, owing to the nature of the substance, the difficulties attending its purification and separation from other substances of like kind, and the peculiar behavior under the influence of heat. It may be said, however, that the facts point to the conclusion that when orthosulphobenzoic acid is heated with either 4 or 6 molecules of resorcinol, a condensation-product containing *six* resorcinol residues is obtained.

With the desire to determine if the hexaresorcinol-derivative of orthosulphobenzoic acid is the only product of the action of resorcinol on the acid, an experiment was made in which a smaller proportion of resorcinol was used than in the preceding experiments. In this case only 2 molecules of resorcinol were used. The experiment was performed in a manner entirely similar to the preceding, and the product obtained had the same general appearance and similar properties to that previously described. Upon making an analysis, however, it was soon apparent that this was a different substance, thus:

I. 0.1690 gram substance gave 0.4060 gram CO_2 and 0.0671 gram H_2O.

II. 0.1701 gram substance gave 0.0697 gram $BaSO_4$ (Liebig).

III. 0.3434 gram substance, heated for four hours at 150°, lost 0.0101 gram H_2O.

The figures thus obtained agree very closely with those calculated for a product containing *four* resorcinol residues, but containing less water than that described by Fahlberg and Barge:

	Calculated for $C_{31}H_{20}O_8S+4H_2O$ (Fahlberg and Barge).	Calculated for $C_{31}H_{20}O_8S+H_2O$.	Found. I.	II.	III.
C	59.60	65.24	65.52	...	...
H	4.50	3.86	4.42	...	...
S	5.13	5.62	...	5.63	...
H_2O	11.54	3.16	...	...	2.94

In regard to the constitution of the tetraresorcinol derivative as well as of the hexa derivative, it seems idle at present to speculate. It is, of course, quite possible to assign places to the resorcinol residues in the molecule, but the experimental data are not as yet sufficient to make that kind of speculation profitable.

Summary.

It appears from the foregoing:

1. That when sulphonfluoresceïn is treated with bromine, the chief product of the action is the formation of a dibromine substitution-product.

2. That phosphorus pentachloride causes the substitution of chlorine for the two hydroxyl groups and for the anhydride oxygen in sulphonfluoresceïn.

3. It is not possible to prepare sulphonfluorescein by the action of resorcinol on orthosulphobenzoic acid, but when action takes place between these 2 substances, either 4 or 6 residues of resorcinol enter into the combination according to the circumstances.

VI.—Sulphonphthaleïns Derived from Orthosulpho-paratoluic Acid.[1]

By Walter Jones.

The starting-point in these experiments was methylsaccharin that had been placed at the disposal of Professor Remsen by the "Badische Anilin- und Soda-fabrik."[2] The methylsaccharin was first converted into the corresponding acid ammonium salt by boiling it with dilute hydrochloric acid.

For the purpose of preparing methyldioxybenzoylbenzenesulphonic acid the finely powdered, dry salt is placed with resorcinol (1 mol. acid to 2 mols. resorcinol) in a large test-tube which is in turn immersed in a bath of sulphuric acid. The temperature of the bath is gradually raised, while the contents of the tube are continually stirred with a thermometer. At 100° the resorcinol melts to a dark-red liquid, and the ammonium salt sinks to the bottom. At 160° the ammonium salt dissolves, but no reaction takes place until the temperature rises above 185°. By heating at this temperature for a few minutes, a bubbling begins, due to the escape of water formed in the reaction, and a yellow line is seen on the side of the tube where the thermometer touches in stirring. The entire liquid soon becomes a paste of yellow crystals, and if the stirring be now discontinued, no further reaction can be made to take place, however long the heating be continued, but by stirring the viscous material for about fifteen minutes it becomes almost solid. The whole process requires about forty minutes if the stirring is not stopped, this being a necessary condition for the completion of the reaction.

After cooling, the light-yellow crystalline mass is extracted with water, and the dark-red solution thus obtained is filtered. On evaporating and cooling the solution, a poorly crystalline

[1] From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1891.

[2] See also Randall: This Journal, **13**, 256; and Lyman: *Ibid.* **16**, 513.

yellow material is deposited, and the mother-liquor contains a viscous substance which prevents any further deposition upon subsequent evaporation. If, however, alcohol is added, a further yield may be obtained. The yellow color may be removed from the crystals by boiling the water-solution with animal charcoal and crystallizing repeatedly; but a more convenient way is to treat the yellow material with successive small portions of cold alcohol, in which the coloring-matter is easily soluble, and a separation can thus be effected by filtration. By dissolving the colorless material thus obtained in a large excess of hot alcohol, and allowing the solution to evaporate slowly, crystals of considerable size and of great perfection can be obtained. As this process involves a loss by creeping, and as the supply of material at hand was limited, a saturated water-solution of the salt was placed in a sulphuric-acid desiccator and small crystals thus gradually obtained. The analysis of these crystals gave the following results:

0.2955 gram salt gave 0.1246 gram H_2O and 0.5626 gram CO_2.

0.3910 gram salt gave 0.1663 gram H_2O and 0.7400 gram CO_2.

0.2364 gram salt gave 0.1695 gram $BaSO_4$.

0.2713 gram salt gave 0.1959 gram $BaSO_4$.

	Calculated for $C_{14}H_8SO_4N$.	Found. I.	II.	III.	IV.	V.	VI.
C	51.67	51.92	51.61	....	....	....	....
H	4.63	4.69	4.73	....	....	....	....
S	9.86	....	....	9.85	9.92	....	....
N	4.32	....	....	....	....	4.19	4.20

These analyses show that the reaction which gave rise to this compound must have taken place according to this equation:

$$C_6H_3(CH_3)\begin{cases}CO.OH\\SO_2.ONH_4\end{cases} + C_6H_4(OH)_2 =$$

$$C_6H_3(CH_3)\begin{cases}CO.C_6H_3\begin{cases}OH\\OH\end{cases}\\SO_2NH_4\end{cases} + H_2O.$$

The existence of a basic lead salt of dioxybenzoylbenzenesulphonic acid, which is quite insoluble in water, suggested the corresponding salt of this acid as a possible means of ob-

taining the acid itself. A water-solution of the ammonium salt was boiled with finely powdered minium. The solution should be concentrated and the vessel open to allow an escape of ammonia, otherwise the reaction is very slow. The basic lead salt thus formed is light, and can be almost completely separated from the excess of minium by decantation, the latter being heavy and adhering to the bottom and sides of the vessel. The decanted liquid, which contains an amount of the ammonium salt, is filtered off, and the precipitate obtained on the filter has a light flesh color, owing doubtless to the inclusion of traces of finely-powdered lead oxide. If, however, the material is dissolved in dilute acetic acid and boiled with animal charcoal, large colorless crystals can be obtained without difficulty. Although the solution in acetic acid has always a red color, yet the salt deposited from the concentrated solution is colorless, and as the deposition continues the solution itself gradually loses its color. The salt loses 11 molecules of water at 105°, and a twelfth at 135°, and the completely dehydrated material has a yellow color. The analysis of this salt is in accordance with the formula given below, and as no other formula can be suggested that will accord so well as this one with the analytical results obtained, it has been thought extremely probable:

$$\begin{matrix} HO \\ HO \end{matrix}\!\!>\!C_6H_3.CO.C_6H_3\!<\!\begin{matrix} CH_3 \\ SO_3O \end{matrix}\!\!>\!Pb$$
$$\begin{matrix} HO \\ HO \end{matrix}\!\!>\!C_6H_3.CO.C_6H_3\!<\!\begin{matrix} SO_3O \\ CH_3 \end{matrix}$$
$$Pb\!<\!\begin{matrix} O \\ O \end{matrix}$$
$$\begin{matrix} HO \\ HO \end{matrix}\!\!>\!C_6H_3.CO.C_6H_3\!<\!\begin{matrix} CH_3 \\ SO_3O \end{matrix}\!\!>\!Pb \qquad +12H_2O.$$
$$\begin{matrix} HO \\ HO \end{matrix}\!\!>\!C_6H_3.CO.C_6H_3\!<\!\begin{matrix} SO_3O \\ CH_3 \end{matrix}$$

The lead was determined by igniting in a porcelain crucible with sulphuric acid. The analytical results are as follows:

0.3163 gram of the salt gave 0.0298 gram H_2O at 105°, 0.0330 gram H_2O at 135°, and 0.1396 gram $PbSO_4$.

0.4736 gram of the salt gave 0.0440 gram H_2O at 105°, 0.0504 gram H_2O at 135°, and 0.2072 gram $PbSO_4$.

0.6015 gram of the salt gave 0.0567 gram H_2O at 105°, 0.0625 gram H_2O at 135°, and 0.2654 gram $PbSO_4$.

	Calculated.	Found. I.	II.	III.
$11H_2O$	9.60	9.42	9.29	9.43
$12H_2O$	10.47	10.43	10.64	10.39
Pb	30.08	30.14	29.88	30.13

When all the acetic-acid mother-liquors were brought together they were boiled with lead oxide for the purpose of getting rid of the large excess of acetic acid present. The basic lead salt was decanted as before, but on filtering off the liquid there separated from the filtrate, as it touched the cold flask, a yellow powder in considerable quantity. This powder was found to be soluble in hot water but could not be crystallized from the solution, always falling as a fine crystalline powder when the solution cooled. The salt loses its water of crystallization so easily that it was found impossible to determine it, and the lead determinations were made from the completely dehydrated salt. The analyses given below correspond to the composition represented by the formula

$$Pb\begin{matrix}/O\backslash\\\backslash O/\end{matrix} C_6H_3.CO.C_6H_3\begin{matrix}/CH,\\\backslash SO_2O.Pb.OH\end{matrix}$$

0.3408 gram of the salt gave 0.2828 gram $PbSO_4$.
0.2163 gram of the salt gave 0.1797 gram $PbSO_4$.

	Calculated.	Found. I.	II.
Pb	56.22	56.66	56.73

It was difficult to obtain the acid in pure condition, owing to its extreme solubility in water. Alcohol was tried, but with no more successful result. A solution of the pure basic lead salt, in as little acetic acid as would dissolve it, was completely precipitated with sulphuretted hydrogen, and the lead sulphide filtered off. The solution was then evaporated almost to dryness before any crystallization took place, and the material had a decidedly reddish-brown color, due probably to decomposition caused by the continued heating which was necessary to expel the last traces of acetic acid. In order to avoid the use of acetic acid, some of the pure basic lead salt was ground fine in an agate mortar, and sulphuretted hydrogen passed through a suspension of the powder in water. After the lead sulphide had been filtered off the solution was evaporated, as before, on a water-bath. When the liquid be-

came viscous, spherical aggregates began to separate, and the heating was discontinued. After the material had stood for a few days, the vessel contained a solid mass of beautifully crystalline acid, and on the sides of the vessel was a most delicate pink tinge. The liquid acid which was allowed to stand for crystallization was of a light straw color, but the crystals were colorless. The easy decomposition of this acid by heat prevented accurate determinations of its water of crystallization. The analysis, however, for carbon, hydrogen, and sulphur showed that it has the formula

$$C_6H_3(CH_3)\begin{cases}CO.C_6H_3\begin{cases}OH\\OH\end{cases}\\SO_3OH\end{cases}+4H_2O.$$

0.1227 gram acid gave 0.0757 gram $BaSO_4$.

0.2279 gram acid gave 0.1418 gram $BaSO_4$.

0.1416 gram acid gave 0.0646 gram H_2O and 0.2294 gram CO_2.

0.1319 gram acid gave 0.0586 gram H_2O and 0.2158 gram CO_2.

	Calculated.	Found. I.	II.	III.	IV.
S	8.44	8.48	8.55	....	....
C	44.20	....	....	44.50	44.62
H	5.27	....	....	5.11	4.94

Barium Salt, $\left(C_6H_3(CH_3)\begin{cases}CO.C_6H_3(OH)_2\\SO_3\end{cases}\right)_2Ba+5H_2O$.—This salt crystallizes from its water solution in small but well defined crystals. When the crystallization occurs from a very concentrated solution, the crystals form spherical aggregates having a beautiful satin lustre when broken. In an experiment, which will be described later, some crystals of this salt were obtained of a size which would admit of measurement. When examined under the microscope two forms could be clearly distinguished. The large crystals seemed to have rhombohedral faces, while the small radially concentric tufts appeared as tetragonal prisms. As the faces were mottled by impurity unequally distributed, and besides very much curved, no measurements were made. The analysis of the salt gave the following results:

0.2866 gram of the salt gave off 0.0315 gram H_2O and yielded 0.0786 gram $BaSO_4$.

0.2721 gram of the salt gave off 0.0298 gram H_2O and yielded 0.0748 gram $BaSO_4$.

0.1943 gram of the salt gave off 0.0207 gram H_2O.

	Calculated.	Found. I.	II.	III.
$5H_2O$	10.70	11.00	10.98	10.65
Ba	16.30	16.13	16.17	....

Calcium Salt, $\left(C_6H_3(CH_3)\begin{matrix}CO.C_6H_3(OH)_2\\SO_3\end{matrix}\right)_2 Ca+6H_2O$.—This salt forms a crystalline mass.

0.3303 gram of the salt gave off 0.0452 gram H_2O and yielded 0.0591 gram $CaSO_4$.

0.2791 gram of the salt gave off 0.0374 gram H_2O and yielded 0.0494 gram $CaSO_4$.

	Calculated.	Found. I.	II.
$6H_2O$	14.19	14.00	13.88
Ca	5.25	5.26	5.24

Neutral Lead Salt, $\left(C_6H_3(CH_3)\begin{matrix}CO.C_6H_3(OH)_2\\SO_3\end{matrix}\right)_2 Pb+7H_2O$.—The easy formation of two perfectly stable basic lead salts by heating a solution of the ammonium salt with lead oxide would lead to the belief that these are the forms in which lead would be likely to occur in combination with this acid. Yet when a warm-water solution of the acid is treated with lead carbonate, the compound formed is the neutral lead salt, which shows no tendency to pass over into either of the basic salts even when its solution is boiled. The salt cannot be obtained in definite crystal forms, owing to its easy solubility in water, but separates as a gelatinous paste from extremely concentrated solutions. This paste, however, is easily soluble in water, showing that no conversion has taken place into either of the basic salts.

0.2871 gram salt gave 0.0386 gram H_2O and 0.0937 gram $PbSO_4$.

0.2246 gram salt gave 0.0296 gram H_2O and 0.0737 gram $PbSO_4$.

	Calculated.	Found. I.	Found. II.
$7H_2O$	13.30	13.47	13.19
Pb	21.85	22.29	22.40

Zinc Salt, $\left(C_6H_3(CH_3)\begin{matrix}CO.C_6H_3(OH)_2\\SO_3\end{matrix}\right)_2 Zn + n.H_2O$. —

This salt could only be separated from its water solution by drying for a long time in a sulphuric-acid desiccator. The material thus obtained did not contain water of crystallization, although this might have been lost in the process of drying. The substance which was analyzed was of a dark red color and probably partly decomposed, yet the material contained just the amount of zinc required to form a zinc salt of this acid.

0.1969 gram of the salt gave 0.0463 gram $ZnSO_4$.

0.2489 gram of the salt gave 0.0592 gram $ZnSO_4$.

	Calculated.	Found. I.	Found. II.
Zn	9.60	9.51	9.62

Silver Salt, $C_6H_3(CH_3)\begin{matrix}CO.C_6H_3(OH)_2\\SO_3Ag\end{matrix} + 2H_2O$. — Considerable difficulty was experienced in preparing this salt, owing to its sensitiveness to light. It can be made to crystallize in fine large crystals if the solution is concentrated on a water-bath, but the heating necessary for this evaporation always turns the liquid a dark color. A specimen of the salt prepared by treating a cold water solution of the acid with pure silver carbonate was placed in a desiccator and protected from the light. Although the utmost care was taken to prevent decomposition of the salt, nevertheless the liquid soon became dark, and it was thought advisable to remove the few colorless crystals that had formed. The water of crystallization is given off on exposure to the air, some of the small crystals having lost their lustre at the beginning of the analysis. The silver was determined as the metal by igniting the salt and then evaporating with nitric acid.

0.1528 gram salt gave 0.0118 gram H_2O and 0.0365 gram Ag.

	Calculated.	Found.
$2H_2O$	7.98	7.72
Ag	23.93	23.90

The free acid was treated with acetic anhydride, but even at the boiling temperature of the anhydride no transformation into an acetyl product could be effected.

When the free acid is treated with phosphorus pentachloride, even as high as 120°, the free acid was recovered from the mass after treatment with water, thus showing that the two hydroxyl groups in the resorcinol residue could not have been displaced by chlorine.

Preparation of Paramethylsulphonfluoresceïn, $C_{20}H_{14}O_7S$.—A quantity of paramethyldioxybenzoylbenzenesulphonic acid is placed in a test-tube and the tube is immersed in a sulphuric-acid bath, which is gradually heated to a temperature of 170°. As the temperature of the bath rises the contents of the tube are occasionally stirred with a thermometer. The acid melts at about 130° to a deep-red liquid, and water-globules condense on the upper and colder part of the tube. After heating about an hour at 170° the material in the tube, which is light brown in color, becomes perfectly solid, and if the tube is now removed from the bath and plunged into cold water the material loosens from the sides of the tube and can be removed without difficulty. The products of the reaction are filtered with the aid of a pump and thoroughly washed. The paramethylsulphonfluoresceïn, thus freed to a great extent from impurities, is dissolved in caustic potash, in which it forms a solution of a surprising yellow-green fluorescence. The compound is then precipitated with sulphuric acid, and washed on a filter until the washings give no cloud with barium chloride. The process of washing is an extremely tedious one, requiring the greater part of three days to wash as much as was obtained in this experiment (about 0.600 gram); so that in all subsequent experiments the washing was done in a cylinder by decantation. While this material, as well as most of that which was subsequently obtained, was of a light brown color, products were sometimes obtained of a dark red material of the same chemical composition and, as far as could be determined, possessing the same properties as the lighter material. The analysis of the compound gave the following results :

0.0780 gram hydrous compound gave 0.0037 gram H_2O.

0.0940 gram hydrous compound gave 0.0043 gram H_2O.

0.2261 gram anhydrous compound gave 0.1360 gram $BaSO_4$.

0.2411 gram anhydrous compound gave 0.1521 gram $BaSO_4$.

0.1380 gram anhydrous compound gave 0.0519 gram H_2O and 0.3190 gram CO_2.

0.0914 gram anhydrous compound gave 0.0309 gram H_2O and 0.2125 gram CO_2.

	Calculated for $C_{20}H_{14}O_6S+H_2O$.	Found. I.	II.	III.	IV.	V.	VI.
H_2O	4.50	4.74	4.57	....	....	....	....
S	8.39	....	....	8.26	8.67	....	....
C	62.81	....	....	....	....	63.04	63.39
H	3.67	....	....	....	....	4.18	3.76

The water with which the material was first washed was treated with barium carbonate and partly decolorized with animal charcoal. The liquid was slightly fluorescent, but good crystals were deposited on cooling the concentrated solution, which gave the following analytical results:

A specimen heated to 160° lost no weight.

0.1663 gram of the salt gave 0.1084 gram $BaSO_4$.

0.0850 gram of the salt gave 0.563 gram $BaSO_4$.

	Calculated for $C_6H_3(CH_3)<\begin{matrix}SO_3\\CO_2\end{matrix}>Ba$.	Found. I.	II.
Ba	39.03	39.04	38.96

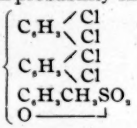
These analyses show that the reaction giving rise to the formation of paramethylsulphonfluorescein is to be represented by this equation:

2. $C_6H_3.CH_3.<\begin{matrix}CO.C_6H_3<OH\\SO_2OH\end{matrix}OH$

$$= C\begin{cases} C_6H_3<\begin{matrix}OH\\O\end{matrix} \\ C_6H_3<\begin{matrix}OH\\C_6H_3.CH_2.SO_2\end{matrix}O \end{cases} + C_6H_3.CH_3.<\begin{matrix}COOH\\SO_2OH\end{matrix} + H_2O.$$

Treatment of Paramethylsulphonfluorescein with Phosphorus Pentachloride.—Molecular quantities of these two substances were heated in a sulphuric-acid bath to 140°, and as the reaction proceeded small portions of phosphorus pentachloride were

added. When the evolution of gases had ceased the flask containing the products of the reaction was cooled and the material washed with water. This reddish-brown substance was found by a microscopic examination to consist of tolerably well-crystallized red grains. These crystals were soluble in alkali, with a dark-blue color and without fluorescence. Analysis of the compound corresponded to the composition of the fluoresceïn in which four chlorine atoms are introduced, and which in all probability should be represented by the formula,



0.6225 gram crystallized compound gave 0.0839 gram H_2O.

0.2215 gram anhydrous compound gave 0.4020 gram CO_2 and 0.0598 gram H_2O.

0.1687 gram anhydrous compound gave 0.0829 gram $BaSO_4$.

0.1011 gram anhydrous compound gave 0.0478 gram $BaSO_4$.

0.1160 gram anhydrous compound gave 0.1360 gram AgCl.

	Calculated.	Found. I.	II.	III.	IV.	V.
$4H_2O$	13.19	13.48	....	....	....	....
C	50.64	....	50.00	....	....	....
H	2.54	....	3.00	....	....	....
S	6.76	....	....	6.79	6.48	....
Cl	29.94	....	....	....	....	29.01

Treatment of Paramethylsulphonfluoresceïn with Bromine.—According to the directions given by Von Baeyer for the preparation of eosin, this compound was suspended in 4 times its weight of glacial acetic acid, and a 20-per cent. solution of bromine in glacial acetic acid added until enough bromine had been used to form a tetra-bromine substitution-product (8 equivalents). The mass was filtered, washed with glacial acetic acid, and then thoroughly washed with water. As this product was found to contain only a trace of bromine, perhaps mechanically held, the experiment was repeated in a flask so that the materials could be shaken together. Twice the necessary amount of bromine was added, and the mixture,

after having been shaken at intervals during an hour, was allowed to stand over night. It was washed with glacial acetic acid, which was driven off by continued heating on a water-bath, the washing with water having been omitted to avoid loss on account of the slight solubility of the material. The compound in alkaline solution has a beautiful eosin fluorescence, and was found on analysis to be an impure dibromparamethylsulphonfluoresceïn.

0.1969 gram hydrous compound gave 0.0114 gram H_2O.

0.1918 gram hydrous compound gave 0.2878 gram CO_2 and 0.0547 gram H_2O.

0.1633 gram hydrous compound gave 0.0693 gram $BaSO_4$.

0.1843 gram hydrous compound gave 0.0736 gram $BaSO_4$.

0.1845 gram hydrous compound gave 0.1201 gram AgBr.

	Calculated for $C_{20}H_{12}SO_4Br_2.2H_2O$.	Found. I.	II.	III.	IV.	V.
H_2O	6.25	5.80	....	....	....	....
C	41.68	....	40.93	....	....	....
H	2.79	....	3.17	....	....	....
S	5.56	....	....	5.32	5.52	....
Br	27.76	....	....	....	....	27.92

Treatment of Orthosulphoparatoluic Acid with Larger Proportions of Resorcinol.—When the acid and resorcinol, in the proportion of 1 molecule of the former to 2 molecules of the latter, are allowed to act on each other, a sulphonphthaleïn is formed which contains four resorcinol residues; and, moreover, when such proportions of the acid and the phenol are employed as should be theoretically required for the formation of this sulphonphthaleïn with four resorcinol residues, there is then formed a sulphonphthaleïn containing six resorcinol residues. This last result is also reached when any excess of the phenol is used over that theoretically required to form the product containing four resorcinol residues. These statements are based on the results of three experiments which are described below. While the analytical results are not good, they are quite as near the theoretical numbers as could be expected in the case of compounds of their physical character. The materials obtained and used for analysis were dark amorphous powders, which in some cases were soluble in water to such an extent as to render their purification from more soluble im-

purities by continued washing impossible. They could not be heated with water because there was always present a substance whose melting-point is very low, and which served at slightly elevated temperatures to cause the entire mass of material to form a viscous liquid. However, in view of the fact that both of these substances possess the remarkable fluorescence which characterizes compounds that belong to the class of phthaleïns, together with the analyses obtained, we can see no objection to regarding them as complex sulphonphthaleïns.

Experiment 1.—Two and a half parts of orthosulphoparatoluic acid and two parts of resorcinol (1 equivalent of the acid and 2 of resorcinol) were placed in a test-tube and heated by means of a sulphuric-acid bath at 160° until the dark-red liquid first formed had solidified, a process which requires about eight hours. From time to time the contents of the tube were stirred with a thermometer, which was kept in the tube during the entire operation.

There was a plentiful evolution of bubbles of water-vapor until near the end of the reaction, when the materials turned jet black and solidified. The products of the reaction were removed from the tube and washed thoroughly with water. The material on the filter was then dissolved in moderately concentrated caustic potash, precipitated from the alkaline solution with sulphuric acid, and washed on a filter until the wash-water showed no cloud when treated with barium chloride. The sulphonphthaleïn thus obtained is a light-brown powder when dry, and shows a beautiful green-red fluorescence in very dilute alkaline solution. The analysis of the sulphonphthaleïn gave the following results:

0.2147 gram hydrous compound gave 0.0197 gram H_2O.

0.2333 gram hydrous compound gave 0.0211 gram H_2O.

0.2734 gram hydrous compound gave 0.1243 gram H_2O and 0.6151 gram CO_2.

0.2112 gram hydrous compound gave 0.1141 gram H_2O and 0.4740 gram CO_2.

0.1822 gram hydrous compound gave 0.0672 gram $BaSO_4$.

0.1314 gram hydrous compound gave 0.0513 gram $BaSO_4$.

	Calculated for $C_{22}H_{22}O_8S.3H_2O$.	Found. I.	II.	III.	IV.	V.	VI.
$3H_2O$	8.66	9.18	9.04	...	...	...	...
H	4.53	...	...	5.05	6.00	...	...
C	61.92	...	...	61.35	61.20	...	...
S	5.17	...	...	...	...	5.07	5.36

Experiment 2.—The method of procedure was the same as in Experiment I, except that 4 equivalents of resorcinol and 1 of the acid were used. The products of the reaction would not completely solidify, although the heating was carried on during two periods of eight hours each, and the material was much more difficult to handle, owing to the presence of a tar-like substance. Analytical results:

0.2721 gram hydrous compound gave 0.0224 gram H_2O.

0.2004 gram hydrous compound gave 0.0167 gram H_2O.

0.1821 gram hydrous compound gave 0.0829 gram H_2O and 0.4303 gram CO_2.

0.1322 gram hydrous compound gave 0.0585 gram H_2O and 0.3091 gram CO_2.

0.1570 gram hydrous compound gave 0.0467 gram $BaSO_4$.

0.1540 gram hydrous compound gave 0.0453 gram $BaSO_4$.

	Calculated for $C_{44}H_{38}O_{10}S.4H_2O$.	Found. I.	II.	III.	IV.	V.	VI.
$4H_2O$	8.88	8.23	8.33	...	...	...	...
C	64.21	...	...	64.45	63.77	...	...
H	4.63	...	...	5.05	4.92	...	...
S	3.90	...	...	...	...	4.09	4.04

Experiment 3.—In this experiment 6 equivalents of resorcinol and 1 equivalent of the acid were used. During the heating the evolution of water-vapor was at times so violent that it was feared the material in the tube would be raised to the top. The product obtained in this reaction was much more troublesome than that obtained in either of the two experiments described. After the tube had cooled the contents were powdered in an agate mortar, but as soon as wash-water was applied the material formed a gelatinous mass which could only be imperfectly washed. The analyses of the product obtained gave the following results:

0.2572 gram hydrous compound gave 0.0209 gram H_2O.

0.3201 gram hydrous compound gave 0.0263 gram H_2O.

0.2211 gram hydrous compound gave 0.1053 gram H_2O and 0.5139 gram CO_2.

0.1818 gram hydrous compound gave 0.0479 gram $BaSO_4$.

0.1249 gram hydrous compound gave 0.0303 gram $BaSO_4$.

0.3526 gram anhydrous compound gave 0.1395 gram H_2O and 0.9024 gram CO_2.

	Calculated for $C_{44}H_{30}O_{10}S.4H_2O$.	I.	II.	Found. III.	IV.	V.	VI.	Calculated for $C_{44}H_{30}O_{10}S$.
$4H_2O$	8.88	8.13	8.22	...	...	...	...	...
C	64.21	...	...	63.38	...	...	69.79	70.39
H	4.63	...	...	5.29	...	....	4.39	4.01
S	3.90	...	...	...	3.63	3.33	...	4.28

Owing to a lack of time no attempts were made to obtain derivatives of these compounds. Although the sulphonphthaleïns as a rule are not compounds that can easily be obtained in pure condition, yet it is not at all impossible that these complex bodies may yield derivatives which will admit of more accurate analytical results than are here given.

Summary.

The results which have been reached in the course of the work described are in brief these:

1. When acid ammonium orthosulphoparatoluate is heated with resorcinol, the ammonium salt of paramethyldioxybenzoylbenzenesulphonic acid is formed.

2. The acid itself can be obtained by treating the ammonium salt with lead oxide and subsequently precipitating the lead with hydrogen sulphide.

3. The phenol-hydroxyl groups of the acid could not be replaced by residues of other acids.

4. The heating of the acid causes the formation of paramethylsulphonfluoresceïn.

5. All four hydroxyl groups of hydrous paramethylsulphonfluoresceïn can be replaced by chlorine.

6. The product obtained by treating paramethylsulphonfluoresceïn with an excess of bromine is a dibromine substitution-product which possesses the characteristic fluorescence of eosin in dilute alkaline solution.

7. Two other sulphonphthaleïns can be derived from orthosulphoparatoluic acid by treating it with resorcinol; one containing 4 and the other 6 resorcinol residues.

A STUDY OF THE CHEMICAL BEHAVIOR OF AMMONIA TOWARD FERRIC CHLORIDE AND FERROUS CHLORIDE[1].

BY ALFRED S. MILLER.

I. Conduct of Ammonia towards Ferric Chloride.

According to Rogstadius:[2]

1. Dry ammonia gas is not absorbed by ferric chloride at ordinary temperatures.

2. The action of ammonia gas is first a reduction of the ferric chloride to ferrous chloride.

According to H. Rose:[3]

1. The ferric chloride absorbs dry ammonia gas *without alteration of the external appearance.*

2. The formula for the compound is $Fe_2Cl_6.2NH_3$.

3. The compound deliquesces in the air.

4. When thrown into water in considerable quantities, it dissolves with a hissing noise.

These statements are not sustained by the experiments which are given here.

The ferric chloride was made by heating, in a combustion tube, iron wire in a stream of dry chlorine gas. The ferric chloride was deposited, in the cool part of the tube, in dark green crystalline scales. These scales were sublimed in a stream of dry chlorine gas, and cooled in the same gas; after which the free chlorine was swept out by dry air. The tube was then broken beyond the place where the wire had been placed, to prevent any carbon or other residue of the wire from mixing with the ferric chloride while removing the latter from the tube. On account of the extremely deliquescent nature of the ferric chloride, it is difficult to transfer it from one container to another without absorbing moisture.

Analysis:

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[1] Extract from a thesis presented to the Faculty of the Post-graduate Department of Heidelberg University (Ohio), for the degree of Doctor of Philosophy.

[2] J. prakt. Chem., 86, 307.

[3] Ann. der phys. Pogg., 24, 302.

	Per cent. obtained.	Calculated.
Cl	65.49	65.51
Fe	34.51	34.49
	100.00	100.00

A rapid stream of dry ammonia gas was passed over this ferric chloride at 20° C. The action was immediate and so violent that in a short time it raised the temperature of about 200 cc. of water, in which the U tube with the ferric chloride had been placed, to 28° C., formed a melted mass through which a white powder was distributed, and a yellow powder was deposited in the cooler part of the tube. The temperature was reduced by changing the water, but, after passing the ammonia for half an hour, the tube burst, either from the heat or pressure produced by the action of the ammonia on the ferric chloride. The white powder was, no doubt, ammonium chloride, and the yellow powder, ammonium chloride colored with iron.

The ammonia was obtained by heating strong aqueous ammonia. The drying apparatus consisted of an empty Woulff bottle surrounded by water to condense any steam that might be carried over, another Woulff bottle filled with small pieces of charcoal, two cylinders filled with sticks of potash, and two tubes filled with lime. A guard tube filled with lime was used to prevent any moisture from coming in from the end of the apparatus.

Ammonia was again passed (more slowly at first) over ferric chloride for two hours, at 18° to 22.5° C. The color of the substance changed slowly to a reddish brown, the change of color being accompanied by a slight evolution of heat. Dry air was passed over this substance, at the end of the experiment, to take out free ammonia.

In analyzing this substance, separate samples were taken to determine the iron, chlorine, and ammonia. In my calculations in these experiments, I have expressed the composition of ferric chloride by the formula $FeCl_3$. Those who prefer to write it Fe_2Cl_6 can easily make the change.

The iron was determined as ferric oxide, the chlorine as silver chloride, and the ammonia was determined volumetrically.

Per cent. obtained.				Calculated for $FeCl_3.2NH_3$.
Fe.	Cl.	NH_3.		
27.87	56.63	17.54	Fe	28.50
28.50	53.20	16.36	Cl	54.15
29.16	58.06		NH_3	17.35
27.67	57.87			
29.65	55.96			100.00
29.93				

These variations indicated that the substance was not homogeneous. Ammonia was passed, about the same length of time, over another sample of ferric chloride with similar results. This substance is less deliquescent than pure ferric chloride, and gave no reaction with potassium ferricyanide.

Ammonia was passed over ferric chloride for a longer time, with the following results:

Passed ammonia over ferric chloride

	Per cent. obtained.			
$2\frac{1}{2}$ hours...	Fe 27.45	9 hours..	Fe 21.96	
	Cl 52.24		Cl 42.77	
	NH_3 19.93		NH_3 35.26	
6 hours....	Fe 22.89	10 hours..	Fe 21.93	
	Cl 43.04		Cl 42.15	
	NH_3 32.26		NH_3 35.44	
7 hours....	Fe 22.31	12 hours..	Fe 20.00	
	Cl 43.27		Cl 38.50	
	NH_3 34.86			

Most of the substance had changed to a red powder and had a strong odor of ammonia. It was evident that some of the ammonia was held either very loosely chemically, or simply by absorption.

Through the manipulation of the substance for so many experiments and determinations, it possibly absorbed a trace of moisture, which enabled it to absorb a little more ammonia than it could have retained if perfectly dry. Air was again passed over the substance and another analysis was made, which showed a loss of ammonia. This was repeated with a similar result. The question now was, how to determine how much of the ammonia was held merely by absorption and how much chemically. The fact that some of the ammonia was given off at ordinary temperatures does not however prove that it was not held chemically. By adding an excess of ammonia to

a solution of cupric sulphate and evaporating the solution, dark blue crystals of *ammonio-cupric sulphate*, $CuSO_4.4NH_3.H_2O$, are deposited. These crystals lose all of their ammonia when exposed to the air, and yet the ammonia is, no doubt, in chemical combination.

Ammonia was passed over ferric chloride for fourteen hours. Dry air was passed over a sample of this while it was slowly heated (to aid the escape of possible free ammonia) at 61° C. This sample no longer gave off any odor of ammonia, and on analysis gave approximately five molecules of ammonia, $FeCl_3.5NH_3$.

Analysis for iron and chlorine:

	Per cent. obtained.
Fe	22.50
Cl	42.97

Ammonia was again passed over ferric chloride for fifteen hours, and dry air was passed over this substance.

		Per cent. obtained.	Calculated for $FeCl_3.5NH_3$.
22 hours....	Fe	22.42	
	Cl	42.22	
26 hours....	Fe	22.47	
	Cl	42.73	
27½ hours...	Fe	22.56	22.62
	Cl	42.86	42.97
	NH_3	34.52	34.41
		99.94	100.00

Approximately the same result was obtained by slightly heating the substance while passing dry air over it for 27½ hours. The air was passed through a solution of potash, then through concentrated sulphuric acid and two tubes filled with lime. The usual guard tube was used, and the air was drawn through the apparatus by an aspirator.

This does not prove that more of the ammonia was not held chemically, but it seems to prove that ferric chloride will hold 5 molecules of ammonia at ordinary temperatures in a perfectly dry atmosphere.

A sample of this substance was placed in a U tube and dry air was passed over it, while the tube was heated to 100° C.

Analysis:

	Per cent. obtained.	Calculated for $FeCl_3.4NH_3$.
Fe	24.30	24.29
Cl	46.16	46.14
NH_3	29.53	29.57
	99.99	100.00

Another sample was treated in the same way for five hours, and gave approximately the same result. The compound, therefore, became at 100° C., $FeCl_3.4NH_3$. A sample heated at 120° C. showed a loss of ammonia of nearly 2 per cent. more.

Another sample was treated in the same way and heated to 200° C., in a paraffin-bath. A yellowish white deposit of ammonium chloride was deposited in the cooler part of the tube.

Analysis for iron and chlorine :

	Per cent. obtained.	Calculated for $FeCl_3.NH_3$.
Fe	30.28	31.21
Cl	56.95	59.29

Below 280° C. the substance was entirely dissociated, leaving a small residue of iron in the ferric condition.

A sample of the compound was placed in water for a week or longer. At the end of this time the substance had not passed into solution, and showed no apparent change. It was filtered off and washed. After being dissolved in nitric acid, it gave no reaction for ammonia nor for chlorine. Both the ammonia and the chlorine were found in the filtrate. Samples placed on a filter and washed with water gave the same results. The compound, when treated with water, evidently gives up its ammonia and its chlorine, and takes up the hydroxyl radicle without going through the processes of solution and reprecipitation.

In order to avoid all possibility of absorption of moisture by the ferric chloride while transferring it from the combustion-tube, in which it was made, to a U tube for the purpose of passing ammonia over it, a combustion-tube was bent, at one end, into a U tube. The ferric chloride was made in the combustion-tube as before, and volatilized in a stream of chlorine gas until it had collected in the U tube. Dry air was then passed through the tube for half an hour, to take out all free chlorine. The ammonia apparatus was then attached to

the tube. Ammonia was passed over this ferric chloride for twenty hours, at 18° to 20° C.

Analysis for iron and chlorine:

	Per cent. obtained.	Calculated for $FeCl_3.6NH_3$.
Fe	21.01	21.16
Cl	40.17	40.20

No air was passed over this substance before removing it from the tube. The slight excess of 0.18 per cent. of ammonia over six molecules, $FeCl_3.6NH_3$, which this analysis indicates, was probably due to free ammonia. The experiment indicates that 6 molecules of ammonia is the maximum saturation-capacity of ferric chloride.

A series of 3 U tubes was arranged, a sample of the substance was placed in each U tube, and dry air was passed through the U tubes, while the first was heated to 100° C., the second to 110°–116° C., and the third to 150°–159° C., for two hours.

Analysis of the third sample:

	Per cent. obtained.	Calculated for $2FeCl_3.5NH_3$.
Fe	27.31	27.36
Cl	51.79	51.99

Analysis of the second sample:

	Per cent. obtained.	Calculated for $FeCl_3.4NH_3$.
Fe	24.23	24.29
Cl	46.49	46.15

The third sample was again heated to 150°–154° C., and dry air at ordinary temperature was passed over it.

Analysis:

	Per cent. obtained.
Fe	27.47
Cl	53.04

A fourth sample was heated to 170° C., for three hours. The first two hours air at ordinary temperature was passed over it, the third hour the air was passed through a tube heated to 100° C., before it reached the substance.

Analysis:

Fe	27.86
Cl	52.89

Above 100° C. the substance began slowly to dissociate.

The chlorine and the ammonia, which were driven off, formed ammonium chloride, part of which was deposited in the cool part of the tube and part in the substance where the temperature was reduced by a stream of air at lower temperature, or by reason of its being removed from the side of the tube to the interior, where the temperature was lower.

It will be noticed that when the third sample was heated to 150°–159° C., and air was passed over it, which had passed through 2 tubes heated to 100°–116° C., more of the ammonium chloride, which formed, was carried out of the substance. When the same sample was treated in the same way except that air was passed over it at ordinary temperature, more of the ammonium chloride collected in the substance, which explains the increase in the weight of chlorine. The weight of chlorine is high in the second sample, which is due to the formation of ammonium chloride.

The following results will show that the ferric chloride absorbs the ammonia very slowly:

Passed ammonia:

		Absorbed.		Temperature.
2	hours	17.54	per cent. NH_3	20°–23° C.
2½	"	19.93	" " "	20°–22° C.
6	"	32.26	" " "	19°–20° C.
7	"	34.86	" " "	18°–22° C.
10	"	35.44	" " "	18°–20° C.

The amount of ammonia does not depend entirely upon the time that the gas is passed over the ferric chloride, but is conditioned also by the temperature, and the rapidity and strength of the stream of the gas. Freshly made ferric chloride takes up the gas faster than that which is a week or so old.

When the ferric chloride has absorbed 6 molecules of ammonia, $FeCl_3.6NH_3$, most of it consists of a red powder.

I have made more than fifty determinations in conducting these experiments. Many of these were made to discover what action had taken place in different stages of the experiments, and would hardly be of interest to the reader. At no stage of the experiments, either in working ammonia into the compound or in taking it out, did it give any reaction with potassium ferricyanide. Ammonia, therefore, does not

reduce ferric chloride as Rogstadius, who has investigated this subject, states.

When the ferric chloride has taken up 6 molecules of ammonia, the compound that is formed is not deliquescent, and is not soluble in water nor in any of the ordinary solvents. The mineral acids dissolve it to a red solution.

Summary.

1. Anhydrous ferric chloride will absorb 6 molecules of ammonia, $FeCl_3.6NH_3$, or $Fe_2Cl_6.12NH_3$, at ordinary temperatures.

2. It will retain 5 molecules of ammonia, $FeCl_3.5NH_3$, in a perfectly dry atmosphere at ordinary temperatures.

3. It becomes $FeCl_3.4NH_3$, at 100° C.

4. The ammonia compound does not dissolve in water: the mineral acids dissolve it to a red solution.

5. It is not deliquescent.

6. The chlorine and the ammonia can be washed out.

7. The compound showed a gradual dissociation, with formation of ammonium chloride, from 100° C. to 280° C.; just below 280° C. it was entirely dissociated.

8. The compound absorbs dry chlorine gas with the evolution of a considerable amount of heat.

II. Conduct of Ammonia towards Ferrous Chloride.

The following methods for making ferrous chloride were tried: 1. By heating iron wire in a stream of dry hydrochloric acid gas; 2. By heating finely divided iron mixed with 3 times its weight of ammonium chloride; 3. By heating finely divided iron mixed with charcoal, in a stream of dry hydrochloric acid gas; 4. By heating ferric chloride in a stream of dry hydrogen. The last of these methods gave the best results.

It was found that ferrous chloride will absorb approximately 6 molecules of ammonia at ordinary temperatures, and form a white powder, $FeCl_3.6NH_3$. These results were also obtained by Rogstadius.[1]

The compound turns brown when it is exposed to the air. It is difficult to keep it from oxidizing.

[1] J. prakt. Chem., 86, 310; Fehling: Handwörterbuch der Chemie, p. 1106.

A sample of the compound was placed *in vacuo* over sulphuric acid for sixteen hours.—

Analysis:

	Found.	Calculated for $FeCl_3.5NH_3$.
Fe	26.01	26.40
Cl	32.51	34.44

Some of the iron was evidently oxidized.

A sample of the compound was put into a glass tube and hydrogen was passed over this sample for an hour, while the tube was heated to 100° C.

	Found.	Calculated for $FeCl_3.2NH_3$.
Fe	34.65	34.78
Cl	43.81	44.05

Another sample was treated in the same way for three hours.

	Found.
Fe	35.08
Cl	44.26

This indicates that it approximates to the formula $FeCl_3.2NH_3$, at 100° C.

Ammonia is more easily absorbed by ferrous chloride than by ferric chloride. The absorption of ammonia is accompanied by the evolution of a considerable amount of heat. A U tube containing ferrous chloride was placed in about 150 cc. of water, and ammonia was passed through the U tube. In twenty minutes the temperature of the water rose from 19° to 24° C.

I take this opportunity to express my gratitude to Dr. John M. Stillman, Professor of Chemistry in the Leland Stanford Junior University, who suggested the work to me, and in whose laboratory the work was done. His ready and willing counsel, and the kindly interest which he manifested in my work, contributed in a large measure to the success of these experiments.

Contribution from the Chemical Laboratory of Harvard College.

LXXXVII.—ACTION OF SODIC ALCOHOLATES ON CHLORANIL. ACETALS DERIVED FROM SUBSTITUTED QUINONES.[1]

By C. Loring Jackson and H. S. Grindley.

Introduction.

During the study of the action of sodic alcoholates, sodium malonic ester, and similar reagents upon tribromdinitrobenzol and related substances,[2] carried on now for some years in this laboratory, it has been observed repeatedly that one of the atoms of bromine is replaced by hydrogen. In all this work, however, the bromine replaced by hydrogen has stood in the meta position to two other atoms of bromine, and, as it was possible that this strange reaction depended on the symmetrical position of the three atoms of bromine, we undertook the study of a substance with a different constitution; and for this purpose selected chloranil, in which no one of the atoms of halogen is in the meta position to two others. While this substance was well fitted for our work, because the atoms of chlorine which it contains can be replaced with comparative ease; on the other hand the action of most of these reagents with it had been already studied by Stieglitz,[3] Ikuta,[4] Kehrmann,[5] and others, and in no case could we find any mention of a direct replacement of chlorine by hydrogen; but still as it was possible that the compounds formed by such a replacement might have been overlooked among the secondary products of some of these reactions, or might be formed under other conditions, we have carried through our experiments. In fact, one of them has proved that, when sodic methylate acts upon chloranil, a reduction takes place, but the hydrogen, instead of replacing chlorine, reduces part of the chloranil to the corresponding tetrachlorhydroquinone. The work with chloranil, therefore, did not throw light on the replace-

[1] The work described in this paper formed a thesis presented to the Faculty of Arts and Sciences of Harvard University for the Degree of Doctor of Science, by H. S. Grindley. It was presented to the American Academy of Arts and Sciences May, 1894.

[2] This Journal, **11**, 93, 541; **12**, 7, 164, 289; **13**, 164; **15**, 607.

[3] This Journal, **13**, 38. [4] Proc. Am. Acad., **26**, 295.

[5] J. prakt. Chem., [2], **40**, 365.

ment of bromine by hydrogen in the tribromdinitrobenzol, because of the presence of the two atoms of quinone oxygen, which seized upon the hydrogen before it could replace the halogen. In the meantime, however, our experiments have led to interesting results of another sort, which are described in this paper.

The action of potassic phenylate on chloranil was the first selected for study, and we found that, if the substances were mixed in proportion of two molecules of the former to one of the latter, the product was dichlordiphenoxyquinone, $C_6Cl_2(OC_6H_5)_2O_2$, which melts at 243°, and gives a hydroquinone melting at 197°–198° when treated with reducing agents. With the object of replacing the two remaining atoms of chlorine we next treated the dichlordiphenoxyquinone with aniline, but instead of acting on the atoms of chlorine this reagent attacked the phenoxy groups, giving dichlordianilidoquinone and phenol, behaving in this respect in the same way as dichlordimethoxyquinone which, Kehrmann[1] found, was converted by treatment with aniline into dichlordianilidoquinone. This action we found was the normal one for our substance: for example, sodium malonic ester gave with the dichlordiphenoxyquinone the dichlorquinonedimalonic ester melting at 132°, discovered by Stieglitz;[2] and, strangely enough, this indirect method of preparing the substance gives a better yield than the direct action of sodium malonic ester on chloranil, for while Stieglitz by this latter method obtained only about 10 per cent., our yield was as high as 27 per cent. The beautiful bright blue sodium salt

$$C_6Cl_2O_2[CNa(COOC_2H_5)_2]_2$$

was obtained, and analyzed; it is stable for a malonic ester salt. The "deep pure violet color, resembling exactly a concentrated solution of potassium permanganate," obtained by Stieglitz, upon the addition of sodic hydrate to the substance, is due, according to our observations, to some decomposition of the salt brought about by an excess of the alkali. The solution of the pure salt has the full blue color of aniline-blue.

Sodic methylate acted on the dichlordiphenoxyquinone like

[1] J. prakt. Chem. [2], **40**, 370.
[2] This Journal, **13**, 38.

the two reagents already mentioned: that is, the two phenoxy groups were replaced by two methoxy groups; but this action was followed by another and more interesting one, which formed a crystalline salt, appearing as a precipitate if the amount of the methyl alcohol used as the solvent was small. Upon the addition of an acid to this salt a white substance was set free having the following formula:

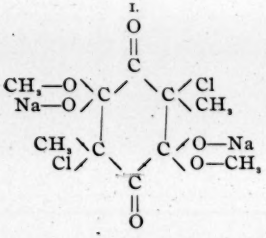
$$C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2.$$

The sodium salt was also analyzed, and proved to have the formula $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$. The two molecules of methyl alcohol appearing in this formula are evidently only alcohol of crystallization, as they could be easily driven off by heat. The corresponding ethyl and methylethyl compounds,

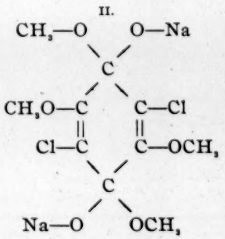
$C_6Cl_2(OC_2H_5)_2O_2(C_2H_5OH)_2$ and $C_6Cl_2(OCH_3)_2O_2(C_2H_5OH)_2$,

were also obtained, and resembled the methyl compound most closely in properties. In considering the way in which the two molecules of methyl alcohol (or sodic methylate) are attached to the molecule of $C_6Cl_2(OCH_3)_2O_2$, only two formulas seemed to us sufficiently probable to merit discussion. In the first of these (I.) the double bonds of the benzol ring are broken, and the radicles NaO and CH_3 added directly to the ring after the manner of the bromine and chlorine addition-compounds discovered by Nef.[1] In the second (II.) the NaO and CH_3 have been added to the two carbonyl groups of the quinone, transforming it into a substance closely related to the acetals.

I.



II.



[1] This Journal, **12**, 483; **13**, 422.

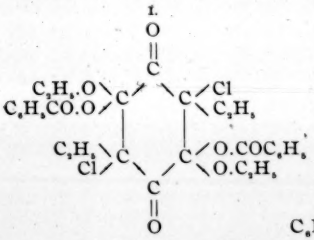
The various isomeric forms of formula I. need not be considered, as the arguments which follow will apply as well to them as to this one. From the properties of this substance, it is not possible to decide between these formulas. It is white, like Nef's bromine addition-products, but an acetal like formula II., would also probably be white, as the colors of chloranil and its derivatives undoubtedly depend on the fact that they are quinones, and in such an acetal as this the quinone nature is obliterated. Its most striking property is the ease with which the free substance loses the two additional molecules of methyl alcohol, since it passes into dichlordimethoxyquinone when heated to temperatures from 160° to 195°; the same change is brought about by dilute sulphuric or hydrochloric acid, slowly in the cold, more rapidly when the mixture is warmed gently. While this instability is in harmony with the second formula given above, it is hard to connect it with the first, as it seems improbable that a methyl group attached directly to the benzol ring, as in formula I., could be so easily removed. It must be remembered in this connection, however, that Stieglitz,[1] by treating the dichlorquinonedimalonic ester with dilute sodic hydrate in the cold obtained parachlorhydroxyquinone, $C_6Cl(OH)H_3O_2$. As in this case carbon atoms attached to the quinone ring were removed by a dilute alkali in a few minutes, it might be that the methyl group in formula I. could be removed under the conditions observed by us. The objection to formula I., mentioned above, might also be met by substituting for it one in which the radicles added were Na and CH_3O instead of NaO and CH_3 as in that formula, but such an addition seems to us at the best improbable. It should be remarked here that Nef's bromine addition-compounds were decomposed with the utmost ease by alkalies, but were very stable in contact with acids, being crystallized from strong nitric acid; our substances show just the opposite behavior, as they are rather remarkably stable toward alkalies; but this difference might be due to the difference in the nature of the radicles added (Br_2 in one case, and NaO and CH_3 in the other) rather than to a difference in the structure of the compounds.

[1] This Journal, 13, 38.

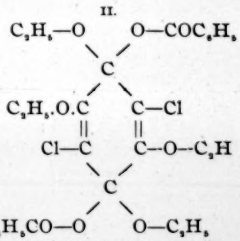
Since, as explained above, the known properties of our new substance were not sufficient to prove the correctness of one or the other of the two formulas proposed, we next turned our attention to some experiments with derivatives of this substance, or rather of the corresponding ethyl compound, which have settled the question conclusively.

To obtain material for this work, which would be possessed of the requisite stability, we replaced the sodium in the salt of our substance with the benzoyl radicle, forming a compound which must have one of the following formulas, according as one or the other hypothesis about these substances is adopted: -

I.



II.



In formula I. the carbonyl groups are unaffected, and the body should therefore retain the properties of a diketone. In formula II., on the other hand, the carbonyl groups having been transformed into acetal groups, the body should have lost its diketone nature. Accordingly, a substance constituted like formula I. should be converted by reducing agents into a substance containing secondary hydroxyl groups, and by the chloride of hydroxylamine into a mon- or dioxime. Upon treating our substance with zinc-dust and glacial acetic acid, (which we have found the most efficient agent for converting quinones into hydroquinones,) it remained entirely unaltered, and the same result was obtained when we tried to act on it with chloride of hydroxylamine. The substance therefore shows neither of these characteristic reactions of the diketones and must be constituted according to formula II. To meet the not overstrong objection that the diketone prop-

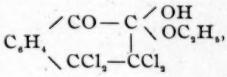
erties of the substance might have been weakened or destroyed by the presence of radicles attached to the ring, we treated dichlordiethoxyquinone with the reducing mixture, and also with chloride of hydroxylamine, and in both cases obtained a satisfactory quinone reaction. We tried also to determine the constitution of our substance in another way. This consisted in making the dichlordiethoxyquinone tetraethylacetal $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$ by replacing the sodium in the sodium salt $C_6Cl_2(OC_2H_5)_2(ONa)_2(OC_2H_5)_2$ by ethyl, and then treating this dissolved in chloroform with bromine in the hope of making an addition-product similar to those of Nef. The result of this experiment was negative, as no bromine was taken up, but this cannot be accepted as an argument against formula II., since Nef[1] found that dichlordiethoxyquinone itself gives no addition-product with bromine,—a result which we can confirm. The failure of the tetraethylacetal to form addition-compounds must be ascribed, therefore, to the presence of the two atoms of chlorine and two ethoxy groups attached to the quinone ring, rather than to the absence of double bonds.

It is perhaps worth noting that the formation of these hemiacetals is easily explained by the diketone formula of quinone, but cannot be brought into harmony with the peroxide formula, so far as we can find. Our work, therefore, would have been of value in determining the constitution of quinone if it had been done before this question was finally settled by Nef's proof of the diketone constitution through his work on the action of bromine on argentic chloranilate.[2]

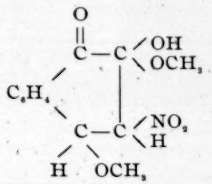
Since, as we have just proved, our new substance has the two molecules of methyl alcohol attached to the two carbonyl groups of the dichlordimethoxyquinone, it belongs to the class of acetals, and we propose to call it and similarly constituted bodies hemiacetals, because only half of the hydrogen in the hypothetical mother-group of the acetals, $=C=(OH)_2$, has been replaced by the organic radicle. Such hemiacetals are not especially uncommon, the most familiar examples being the alcoholates of ordinary chloral and of butylchloral. Jacobsen,[3]

[1] This Journal, **11**, 20. 24. [2] *Ibid.* **12**, 466.
[3] Ber. d. chem. Ges., **4**, 215.

and later Renard,[1] claimed that they obtained the corresponding compound of acetaldehyde, $CH_3CH(OH)(OC_2H_5)$, but do not agree in regard to its boiling-point, and apparently assign to it a much greater stability than would be expected in such a substance. Without multiplying examples, we pass at once to some compounds more nearly related to ours, recently obtained by Zincke with some of his scholars. Zincke and Arnst,[2] by the action of alcohol on tetrachlordiketohydronaphthalin have obtained a compound,



which is tolerably stable in the cold, but decomposes by heat, like our hemiacetal. The corresponding para compound formed no such derivative. Zincke and Neumann,[3] by the action of alcohol on nitro-β-naphthoquinone, obtained a substance the formula of which was made out as follows:

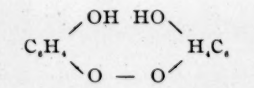


Still later, Zincke and Schaum[4] have made similar compounds from the isomeric heptachlorketotetrahydrobenzols by the action of sodic methylate. Although Zincke's work shows that ring-ketones, orthodiketones, and orthoquinones are capable of forming such hemiacetals; so far as we can find, our compound is the first of this class to be made from a paraquinone, and the compound of Zincke's which approaches most nearly to it, the orthoquinone derivative, differs from it strikingly, for, whereas in our compound both carbonyls are converted into hemiacetal groups, in Zincke and Neumann's only one of the carbonyl groups is thus affected, and at the

[1] Ber. d. chem. Ges., **8**, 132.
[2] Ann. Chem. (Liebig), **267**, 319.
[3] *Ibid.* **278**, 173.
[4] Ber. d. chem. Ges., **27**, 537.

same time a molecule of sodic methylate is added to the ring by the breaking of a double bond. It should be mentioned here that J. U. Nef[1] has assumed the formation of addition-products of water or hydrochloric acid with the carbonyls of of quinone in explaining the formation of hydroquinone by the action of water,[2] or substituted hydroquinones by the action of hydrochloric acid on quinone;[3] but he supposes that these intermediate products break up immediately, and none of them have been isolated.

The discovery of the hemiacetals of the quinones has suggested to us a possible explanation of the constitution of quinhydrone and the bodies related to it. The most important of these substances are quinhydrone formed from one molecule of quinone and one of hydroquinone; resorcinquinone, from one molecule of quinone and one of resorcin; phenoquinone, from one molecule of quinone and two of phenol; and quinhydronedimethyl ether, from one molecule of quinone and two of the monomethyl ether of hydroquinone. The state of our knowledge of the constitution of these substances is described in the following quotation from a paper on this subject by Nietzki:[4] "Aus vorstehenden Versuchen scheint hervorzugehen, dass das Chinhydron, das Chinonresorcin, blosse Additionsproducte des Chinons mit phenolartigen Körpern sind, und zwar scheint hierbei die Zahl der in letzteren enthaltenen freien Hydroxyle stets den beiden Chinonsauerstoffen zu entsprechen. Eine Formel im Sinne der Structurtheorie lässt sich für diese Körper wohl augenblicklich kaum aufstellen, denn die von Kekulé für das Chinhydron vorgeschlagene Structurformel



lässt sich für die Verbindungen des Chinons mit einwerthigen Phenolen nicht mehr anwenden. Aus dem von O. Hesse

[1] This Journal, **13**, 427; Ann. Chem. (Liebig), **270**, 323; Clark: This Journal **14**, 553.

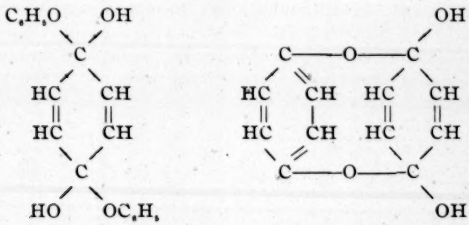
[2] Hesse: Ann. Chem. (Liebig), **220**, 367; Ciamician: Gazz. chim. Ital., **16**, 111.

[3] Levy; Schultz: Ann. Chem. (Liebig), **210**, 133; Sarauw: *Ibid.* **209**, 93.

[4] *Ibid.*, **215**, 136.

beobachtenen Verhalten des Chinhydrons gegen Essigsäureanhydrid scheint jedoch hervorzugehen dass das Chinhydron keine freien Hydroxyle enthält. Auch das von Wichelhaus beobachtete Verhalten des Monomethylhydrochinons spricht dafür, dass Substitutionsproducte des Chinhydrons in den Hydroxylgruppen nicht existiren."

It appears from this quotation that there is no satisfactory theory for the constitution of these compounds, since the statement that they are addition-products amounts to saying that we have no theory on the subject. We would, therefore, advance the following theory in regard to the constitution of these bodies: that they are hemiacetals similar to those described in this paper; in phenoquinone the phenol, in quinhydrone the hydroquinone, taking the place of the methyl or ethyl alcohol, which is added to the substituted quinones in our new substances. On this theory the graphical formulas of phenoquinone and quinhydrone would be written as follows:



The principal arguments in favor of this theory are the following: It requires the union of one molecule of quinone with one molecule of a diatomic phenol such as hydroquinone or resorcin, but with two of a monatomic phenol like common phenol or monomethylhydroquinone, and is in this respect in accordance with the facts. Such substances would not be formed when the hydroxyl groups of the phenols had been converted into alkyloxyl groups, and dimethylhydroquinone has no action on quinone. The products should be unstable, as we have found that the stability of our new hemiacetals depends on the number and strength of the negative radicles at-

tached to the quinone ring, and, in these cases, where there are no negative radicles, we should expect a very slight stability. As a matter of fact, these substances are not only decomposed by acids or alkalies, but quinhydrone even by solution in neutral solvents.[1] The action of acetic anhydride giving diacetylhydroquinone and quinone,[2] which is brought up by Nietzki as a proof of the absence of free hydroxyl, is really in accordance with our theory, as our dimethylhemiacetal with acetic anhydride gave methyl acetate and the quinone from which the hemiacetal was derived. All these observed facts, therefore, are in harmony with our theory. Against it is the marked color of all this quinhydrone group, whereas our hemiacetals are colorless. This may be due, however, to the difference in the nature of the radicles attached to the carbonyl groups, our hemiacetals containing methyl or ethyl, the quinhydrone group aromatic radicles, which might well give more colored compounds. It may be remarked in this connection, that, while the methyl or ethyl ether of resorcin is colorless, the simple resorcin ether itself is reddish brown. An attempt will be made next year to find other parallel cases. Another objection to our theory is, that no salts have been obtained from phenoquinone, whereas the substance, according to our formula, contains two free hydroxyls. Wichelhaus, who states that he obtained no salts of it, adds that the substance turns blue when treated with alkalies; this may indicate the formation of a salt not yet isolated. We have attempted to test our theory by experiment in this direction, but so far with little result. By treating phenoquinone with sodic ethylate, not in excess, we obtained a green salt; but, as much phenol was found in the filtrate, we are inclined to consider this salt at present rather a product of the action of sodic ethylate on the quinone formed by the decomposition, than a salt of the phenoquinone itself. If this interpretation of the observation is true, it has no bearing on our theory, as it shows only that the phenoquinone is easily decomposed by alkalies, this decomposition taking place before it had time to form a salt. We then tried the action of sodic phenylate on

[1] Clark: This Journal, **14**, 574.
[2] Hesse: Ann. Chem. (Liebig), **200**, 248.

quinone, as according to our theory this should act as well, or even better than free phenol, and we have succeeded in getting an action in this case, a strongly colored product being formed; but these experiments were undertaken so late in the year that we had no time to isolate this substance for study. We should add that in the action of potassic phenylate on chloranil, described at the beginning of the experimental part of this paper, there are strong indications of the formation of a diphenylhemiacetal, as the liquid took on a blue-black color in the cold, which upon heating changed to the red of the dichlordiphenoxyquinone. The isolation of this hemiacetal, if possible, will throw a great deal of light upon our theory of the nature of phenoquinone. All these lines of work will be taken up in this laboratory during the next academic year, and we hope that by means of these experiments we shall succeed in testing thoroughly our theory that quinhydrone and phenoquinone are hemiacetals of quinone. The curious addition-compounds of the nitranilines and quinones[1] will also be considered in this connection.

The dichlordimethoxyquinone dimethylhemiacetal

$$C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2,$$

although most conveniently made from the dichlordiphenoxyquinone by the action of sodic methylate, can also be obtained by the action of the same reagent on dichlordimethoxyquinone, or even on chloranil. In this last case the first product is a green sodium salt, which by treatment with water yields the sodium salt of the hemiacetal and the tetrachlorhydroquinone, mentioned at the beginning of this paper. With sodic ethylate and chloranil we have not succeeded in obtaining the corresponding ethyl compound; it may be, however, that this result was due to not finding the proper conditions for the reaction.

The dichlordiethoxyquinone tetraethylacetal

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4,$$

alluded to in the discussion of the constitution of the hemiacetals, was made by the action of ethyl iodide in the cold on the silver salt of the corresponding hemiacetal. The yield was

[1] Hebebrand: Ber. d. chem. Ges., **15**, 1973; Niemayer: Ann. Chem. (Liebig), **228**, 332.

exceedingly small, most of the hemiacetal dropping back to dichlordiethoxyquinone. Its properties were strangely unlike those of the corresponding hemiacetal, for whereas the dichlordiethoxyquinone hemiacetal was essentially insoluble in all solvents, the tetraethylacetal was so easily soluble in all the common solvents except water, that it was hard to crystallize it from any of them. The most striking property of the hemiacetal was its instability, since it gave up ethyl alcohol at temperatures from 140° to 143°, becoming converted into the dichlordiethoxyquinone (melting at 104°–105°); the tetraethylacetal, on the other hand, melts without decomposition at 101°–102°, and from 205° to 275° sublimes apparently unaltered. The hemiacetal is converted into dichlordiethoxyquinone when treated with acids, even more easily than by heat, dilute sulphuric or hydrochloric acid acting on it slowly even in the cold, rapidly when warmed. This is its most marked property; in fact, it is so susceptible to the action of acids that in our earlier preparations we obtained a considerable amount of dichlordiethoxyquinone by drying the hemiacetal at ordinary temperatures, when it had not been washed enough to remove the last traces of acid. In order to bring about a similar decomposition of the tetraethylacetal it is necessary to boil it with sulphuric acid of specific gravity 1.44. A more dilute acid does not act upon it, and even this rather strong sulphuric acid has no action in the cold. With alkalies the hemiacetal forms crystalline salts, which are comparatively stable, since they dissolve in water without decomposition, and can be kept in the dry state for a moderate length of time. The stability of the substance toward alkalies is in marked contrast to its behavior with acids, as it is necessary actually to boil it with sodic hydrate in order to convert it into chloranilic acid. The tetraethylacetal can of course form no salts, as it contains no hydroxyl. It is even more stable toward alkalies than the hemiacetal, as sodic hydrate even when boiling or mixed with alcohol does not decompose it. Finally the hemiacetal is amorphous, the acetal crystallizes finely, so that almost the only property which they have in common is their white color. The salts of the hemiacetals which are not derived from the alkalies are insoluble in water.

The dichlordiethoxyquinone dibenzoyldiethylacetal,

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2,$$

also mentioned in the discussion of the constitution of the hemiacetals, was made by the action of benzoyl chloride on the sodium salt of the corresponding hemiacetal suspended in alcohol. In this case the yield is good, about 66 per cent. of the theoretical, so that this substance is much more accessible than the tetraethylacetal; it crystallizes well, and melts at 170°. It is a curious fact that none of the benzoyl compound is formed, if the sodium or silver salt of the hemiacetal is suspended in ether instead of alcohol, and treated with benzoyl chloride. In order to obtain this benzoyl compound, therefore, it is essential to use alcohol as the diluent. The reaction with ether is apparently the same as that which occurs when the free hemiacetal or its sodium salt is heated to 100° with benzoyl chloride, the products in this case being dichlordiethoxyquinone and ethyl benzoate.

When the dichlordiethoxyquinone dibenzoyldiethylacetal is heated with sulphuric acid of specific gravity 1.44, it is converted into a new substance, the analysis[1] of which gave numbers corresponding to the formula $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2O$. This body must be formed by the saponification of two ethoxy groups by the sulphuric acid, whereas we should have expected that the acid would have attacked rather the two benzoate groups. Our experiments have not as yet given us any means of determining which pair of ethoxy groups has been saponified. From the formula established by analysis we should infer that, after the two ethoxy groups had been converted by saponification into two hydroxyls, a molecule of water was eliminated, leaving the atom of oxygen spanning the benzol ring between two atoms of carbon in the para position to

[1] As our first analytical results approached the numbers calculated for the dichlordiethoxyhydroquinone dibenzoate, $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$, we thought that perhaps we had in hand this substance mixed with an obstinately adhering impurity, and accordingly we made it from the substituted hydroquinone in order to compare it with our substance, but found that the two were not identical, since it melts at 215°, while the melting-point of our new substance is 142°. The bad results from our first analyses we found afterward to be due to the difficulty in securing a complete combustion of our saponification-product, and, after taking special precautions to insure this, numbers were obtained from very carefully purified preparations agreeing excellently with those for the formula given above.

each other. Our substance, therefore, would have some analogy to cineol, if the constitution ascribed to it by Brühl[2] is correct. We realize fully, however, that such an unusual constitution as this should not be considered established without the most convincing proof, and, as at present we are unable to give this, we propose it only as that which accords best with the results of analysis and the method of preparation of the substance. We have made some attempts to prepare derivatives of this substance in order to throw light on its constitution, and have found that hydriodic acid converts it into a substance probably having the formula

$$C_6Cl_2OC_3H_4OH(OCOC_6H_5)_2$$

and melting at 164°, but we have not yet studied this substance thoroughly enough to advance any theory in regard to its constitution. Aniline also forms one or more compounds with the saponification-product, which we have not yet succeeded in bringing into a state fit for analysis. We must content ourselves, therefore, at present with this preliminary statement of our experiments on this subject, the study of which will be continued in this laboratory during the next academic year.

The methyl compounds $C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$, melting at 193°, and $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$, melting at 205°–206°, which agree with the corresponding ethyl compounds in every respect, have also been prepared. In order to determine whether other acid radicles would act like benzoyl, we treated the sodium salt of the diethyl hemiacetal with chlorocarbonic ester, and obtained the dichlordiethoxyquinone diethylacetaldicarbonic ester

$$C_6Cl_2(OC_2H_5)(OC_2H_5)_2(OCOOC_2H_5)_2,$$

which melts at 122°–123°. In view of our experiments with the benzoyl derivative, the saponification of this substance promises interesting results.

We have tried a number of experiments to determine the limits of the formation of hemiacetals from quinones; and have found that the dibromdiphenoxyquinone (melting-point 266°–267°) made from bromanil, forms a hemiacetal, which seems to be as stable as the one made from chloranil. The

[2] Ber. d. chem. Ges., **21**, 461. Compare also **27**, 810.

chlordiphenoxyquinone (melting-point 169°–170°) made from trichlorquinone, also forms a hemiacetal, but this is much less stable than that containing two atoms of chlorine. Even the dimethoxydiphenoxyquinone yielded a hemiacetal, but it was so unstable that it decomposed spontaneously almost as soon as it was formed. So that the stability of the hemiacetals seems to depend on the number and strength of the negative radicles attached to the benzol ring. It was not very probable, therefore, that a hemiacetal of quinone itself could be isolated, but yet we felt it was necessary to try the experiment; and this has established the fact that quinone is acted on by sodic ethylate, although the product—a green salt—has so far, resisted our attempts to purify it for analysis. Work with it is especially hard because of its very slight stability; it takes fire spontaneously, if dried in the air at ordinary temperatures; and although if dried first in hydrogen, it does not take fire on mere exposure to the air, it glows like tinder when heated to temperatures as low as 40°. After we had abandoned, for the present, the attempt to analyze the green salt, we succeeded in throwing some light on its composition by determining the proportion of quinone to sodic ethylate necessary to form it, as we found that each molecule of quinone takes up one molecule of sodic ethylate, but it must be left to future experiments to decide whether the product is really a hemiacetal.

In all the work so far described in this paper, only two of the atoms of chlorine in chloranil have been replaced by other radicles; we found, however, that the other pair of atoms of chlorine could be replaced by phenoxy groups, if the dichlordiphenoxyquinone was treated with sodic phenylate, or if chloranil was acted on by four equivalents of sodic phenylate. The tetraphenoxyquinone thus formed, melted at 229°–230°, and offered a rather striking resistance to the action of reducing agents, although zinc-dust and glacial acetic acid, converted it into tetraphenoxyhydroquinine, $C_6(OC_6H_5)_4(OH)_2$, melting-point 219°–220°. Toward acids the tetraphenoxyquinone shows a marked stability, but by boiling with a strong solution of sodic hydrate, it was converted into the diphenoxanilic acid, $C_6(OC_6H_5)_2(OH)_2O_2$, which melts at about 276°.

Sodic methylate converts tetraphenoxyquinone into the dimethoxydiphenoxyquinone by replacing two of its phenoxy by methoxy groups; the substance melts at 171°. The corresponding diethoxydiphenoxyquinone, melting at 128°, was formed, instead of tetraphenoxyquinone, when chloranil was treated with sodic phenylate made from phenol and sodic ethylate in alcoholic solution. It is a noteworthy fact that bromanil acts differently with sodic phenylate made in this way, giving the dibromdiphenoxyquinone. One other case was observed of the substitution of all four of the chlorine atoms of chloranil. This was when the dichlorquinone dimalonic ester of Stieglitz was boiled with alcohol and sodic carbonate, as it was converted into diethoxyquinone dimalonic ester, melting at 115°. It is certainly strange that such a weak reagent should remove these two atoms of chlorine, which in other cases have seemed very firmly attached to the molecule. In all the reactions just described it is to be observed that the chlorine atoms or phenoxy groups, are replaced in pairs, and this fact also appears in much of the work with chloranil previous to ours. This replacement of the radicles two at a time can probably be connected with the para position of the two atoms of oxygen, which in this case serve to diminish the attraction of these radicles to the benzol ring, and thus make it possible to replace them, as in the case of tribromdinitrobenzol, $CHBrNO_2BrNO_2Br$ (melting-point 192°) where the loosening nitro groups are in the meta position, all three of the bromine atoms are replaced in many reactions.

Experimental Part.

Action of Potassic Phenylate on Chloranil.

In order to study this action, 25 grams of chloranil suspended in 50 cc. of water were treated with an aqueous solution of potassic phenylate, made from 12 grams of potassic hydrate and 25 grams of phenol, which gave the proportion of two molecules of potassic phenylate to one of chloranil. To obtain a good result in this process it was necessary that the chloranil should not be in too large crystals; if, therefore, the specimen used was well crystallized, it was reduced to the hydroquinone with sulphurous acid, and then oxidized with

nitric acid, which left it in a finely divided form easily attacked by the solution of potassic phenylate. The potassic phenylate was added in small portions at a time, and the first few drops imparted to the liquid a chrome-green color, which gradually changed to blue-black as more of the solution was added, until at last the whole became very dark blue or nearly black. In order to complete the reaction the mixture was heated on the steam-bath for thirty minutes, which changed the color from black to red. In the cold there were no signs of the formation of this red substance, but it began to appear as soon as the mixture was warmed. The solution was filtered, and the dark red solid remaining on the filter, after washing thoroughly with water and alcohol, was purified by crystallization from hot benzol until it showed the constant melting-point of 243°.

The analysis of the substance dried at 100° gave the following results:

I. 0.2138 gram substance gave on combustion 0.4692 gram CO_2 and 0.0637 gram H_2O.

II. 0.1510 gram substance gave 0.1206 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_6H_5)_2O_2$.	Found. I.	II.
Carbon	59.83	59.85	
Hydrogen	2.77	3.32	
Chlorine	19.67		19.75

From these results it is evident that the substance is dichlordiphenoxyquinone. The yield is very good, 25 grams of chloranil giving as a rule 26 to 30 grams of the new substance, that is, about 80 per cent. of the theoretical yield.

Properties of Dichlordiphenoxyquinone, $C_6Cl_2(C_6H_5O)_2O_2$.— The substance crystallizes from benzol in beautiful red needles arranged in rosettes. It melts at 243°, and is very slightly soluble in alcohol even when hot, less so when cold; insoluble in cold and in boiling water; difficultly soluble in boiling benzol, and only very slightly soluble in the cold; it is sparingly soluble in cold chloroform, more easily in hot; slightly soluble in cold glacial acetic acid, but easily when the acid is boiling; in ether, ligroïn, carbon disulphide, or acetone, it is insoluble. The three strong acids have no visible effect on it, hot or cold. It is readily saponified by a solution of sodic hydrate, forming chloranilic acid. It is not affected by sul-

phurous acid at 100° under the ordinary pressure, but is easily reduced to the corresponding hydroquinone by warming with hydriodic acid, or by the action of glacial acetic acid and zinc-dust.

Dichlordiphenoxyhydroquinone, $C_6Cl_2(C_6H_5O)_2(OH)_2$.

This substance was prepared by mixing dichlordiphenoxyquinone with hydriodic acid (boiling between 123° and 126°), and heating for some time on the steam-bath. The product formed by this reduction was purified by crystallization from boiling dilute alcohol (50 per cent.) until it showed the constant melting-point of 197°. The analysis of the substance dried at 100° gave the following results:

I. 0.2147 gram substance gave on combustion 0.4678 gram CO_2 and 0.0723 gram H_2O.

II. 0.1578 gram substance gave 0.1244 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_6H_5)_2(OH)_2$.	Found. I.	II.
Carbon	59.51	59.41	
Hydrogen	3.31	3.73	
Chlorine.....	19.56		19.49

The change from the quinone to the hydroquinone is quantitative.

Properties of Dichlordiphenoxyhydroquinone.—It crystallizes from dilute alcohol (50-per cent.) in large colorless prisms, or in little needles very much branched, forming thick aborescent masses which melt at 197°–198°, and are readily soluble in ethyl alcohol, methyl alcohol, or acetone; soluble in carbonic disulphide or hot glacial acetic acid; slightly soluble in chloroform, cold glacial acetic acid, or ether. It is insoluble in water, either cold or hot, benzol, or ligroïn. Dilute or strong sulphuric acid or hydrochloric acid does not act on the dichlordiphenoxyhydroquinone even when hot. It dissolves in alkalies and is reprecipitated from the solution by acids. On long standing or boiling with sodic hydrate it is saponified, giving the sodium salt of chloranilic acid which separates in long dark carmine-red needles.

By the action of oxidizing agents, such as ferric chloride, dilute nitric acid, or potassic dichromate in acid solution, it is easily changed to the corresponding quinone.

Action of Aniline on Dichlordiphenoxyquinone.

The dichlordiphenoxyquinone was treated with aniline in the expectation of removing the two remaining atoms of chlorine. For this purpose 1 gram of dichlordiphenoxyquinone was mixed with 5 grams of aniline, and the mixture warmed on the water-bath for a few minutes. When cool, the large excess of aniline was removed by dilute sulphuric acid, and, after thorough washing, the dark-colored residue was purified by dissolving it in aniline, and then adding a small quantity of alcohol; in this way well-formed dark-brown crystals were obtained, melting at 287°–290°, and therefore probably the dichlordianilidoquinone, the melting-point of which is given as 285°–290°. This substance was first prepared and studied by O. Hesse[1], later by Knapp and Schultz.[2] To confirm this inference the crystals were dried at 100° and the chlorine determined:

0.1480 gram substance gave 0.1174 gram AgCl (Carius).

	Calculated for $C_6Cl_2(C_6H_5NH)_2O_2$.	Found.
Chlorine	19.70	19.61

The reaction therefore took an unexpected course, since the anilido groups replaced the two phenoxy radicles instead of the two atoms of chlorine.

Action of Sodium Malonic Ester on Dichlordiphenoxyquinone.

It has been shown in the preceding section that aniline removes the phenoxy groups instead of the atoms of chlorine from dichlordiphenoxyquinone. We therefore next turned our attention to the action of sodium malonic ester upon it, to see whether this reagent behaved in the same way. In order to study this reaction, 1 gram of dichlordiphenoxyquinone suspended in 10 cc. of absolute alcohol, was treated with a little more than two equivalents of sodium malonic ester, which was made by treating 0.15 gram of metallic sodium with about 10 cc. of absolute alcohol, and then adding 2 grams of malonic ester. On adding the sodium malonic ester, the solution turned very dark-blue, and on standing a dark-blue precipitate separated, which was filtered off and

[1] Ann. Chem. (Liebig), **114**, 306. [2] *Ibid.* **210**, 187.

washed with alcohol, in which it is only slightly soluble. The precipitate dissolved readily in water, with a beautiful blue color, and on the addition of an acid a slightly yellow crystalline product separated, which was purified by recrystallization from boiling dilute alcohol, until it gave the constant melting-point 132°. After drying at 100°, it gave the following results on analysis:

I. 0.2180 gram substance gave on combustion 0.3880 gram CO_2 and 0.0994 gram H_2O.

II. 0.1654 gram substance gave 0.0964 gram AgCl.

	Calculated for $C_4Cl_2[CH(COOC_2H_5)_2]_2O_2$.	Found. I.	Found. II.
Carbon	48.68	48.53	
Hydrogen	4.46	5.06	
Chlorine	14.41		14.41

These results prove that the substance is dichlorquinonedimalonic ester. Four grams of the dichlordiphenoxyquinone gave a yield of about 1.5 grams of the malonic ester compound, that is, 27 per cent. of the theoretical yield.

It is evident that this body must be formed through the replacement of the two phenoxy groups by two malonic-ester radicles and, in fact, it was not hard to detect the phenol, which formed the secondary product of the reaction. For this purpose the alcoholic filtrate from the sodium salt of the malonic-ester derivative, after evaporation nearly to dryness, was diluted with water, and treated with a dilute acid, when the smell of phenol was very evident, and bromine-water gave a voluminous white precipitate. This easy replacement of the phenoxy groups by the malonic-ester radicles, even although the former are attached to a benzol ring, suggests other work in the same line, which will be undertaken in this laboratory.

This dichlorquinonedimalonic ester crystallizes from dilute alcohol in long, slender radiating needles of a yellow color, which melt at 132°, and are insoluble in cold or boiling water, soluble in cold or warm alcohol. It is not affected by weak oxidizing agents, but hydriodic acid reduces it to a white crystalline substance, which melts at 159°–160°, the melting-point of the dichlorhydroquinonedimalonic ester discovered

by J. Stieglitz[1]; our dichlorquinonedimalonic ester is therefore identical with that obtained by him from the direct action of sodium malonic ester on chloranil. Our indirect method of preparing it, however, gives a better yield than the direct method, 27 per cent. instead of 10 per cent. That we might not intrude on this field of research, already occupied by Stieglitz, we have confined our work on this substance to that necessary for establishing its identity.

Sodium Salt of Dichlorquinonedimalonic Ester,

$C_6Cl_2[CNa(COOC_2H_5)_2]_2O_2$.

In order to prepare this salt the dichlorquinonedimalonic ester was dissolved in ether, and treated with rather less than the required amount of sodic ethylate in a strong alcoholic solution. The sodium salt separated at once as a blue precipitate, which was repeatedly washed with ether by decantation, and dried over sulphuric acid and paraffine until the weight remained constant, after which the sodium was determined with the following result:

0.2788 gram salt gave 0.0731 gram Na_2SO_4.

	Calculated for $C_6Cl_2[CNa(COOC_2H_5)_2]_2O_2$.	Found.
Sodium	8.57	8.49

The sodium salt has a beautiful blue color, and is very easily soluble in water, giving a solution of a blue color as intense and striking as that of aniline-blue. It is somewhat soluble in alcohol, but insoluble in ether.

Diethoxyquinonedimalonic Ester,

$C_6(OC_2H_5)_2[CH(COOC_2H_5)_2]_2O_2$.

In the first attempt to form the sodium salt of the dichlorquinonedimalonic ester, the substance was dissolved in absolute alcohol and boiled with an excess of dry sodic carbonate. When the sodic carbonate was first added, the alcoholic solution was colored dark blue; but after filtering out the excess of sodic carbonate and evaporating rapidly, the solution became nearly colorless, and left after the alcohol had been driven off a residue of almost white crystals, which were purified by crystallization from alcohol until the melting-point remained

[1] This Journal, 13, 38.

constant at 115°. The analysis of the substance dried over sulphuric acid and paraffine gave the following results:

0.2010 gram substance gave on combustion 0.4122 gram CO_2 and 0.1242 gram H_2O.

	Calculated for $C_6(OC_2H_5)_2[CH(COOC_2H_5)_2]_2O_2$.	Found.
Carbon	56.25	55.93
Hydrogen	6.25	6.86

It gave no test for chlorine. These results prove that the substance is diethoxyquinonedimalonic ester, and it is certainly strange that this substance should have been formed from the corresponding dichlor compound by the action of sodic carbonate and alcohol, in view of the fact that these two atoms of chlorine in other cases have proved hard to replace. The substance crystallizes in beautiful yellowish white needles melting at 115°, which are insoluble in water, readily soluble in alcohol or ether.

Action of Sodic Methylate on Dichlordiphenoxyquinone—Dichlordimethoxyquinone Dimethylhemiacetal, $C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$.

In order to see whether the phenoxy groups in dichlordiphenoxyquinone would be removed by sodic methylate, as they were when it was treated with sodium malonic ester or aniline, 10 grams of the dichlordiphenoxyquinone were mixed with a methyl-alcohol solution of a little less than four equivalents of sodic methylate, made by treating 2.5 grams of metallic sodium with 60 cc. of methyl alcohol. The solution was warmed gently on the water-bath, and stirred constantly; soon a white crystalline substance began to separate, and the red color of the dichlordiphenoxyquinone disappeared entirely. The solution was filtered, the residue washed with a little alcohol, dissolved in water, filtered again, and then treated with dilute sulphuric acid in excess, which set free a white insoluble compound. The properties of this substance indicated at once that the reaction had not consisted in a simple replacement of the phenoxy by methoxy groups, as in that case the product must have been the dichlordimethoxyquinone discovered by Kehrmann,[1] which is red, melts at 141°–142°, and is

[1] J. prakt. Chem., [2], 40, 370.

not insoluble in the common solvents. To prepare our new body for analysis it was filtered off, washed with water, alcohol, and then with water again; after which it was dissolved in dilute sodic hydrate, filtered, precipitated with dilute sulphuric acid, and washed thoroughly as described above. This treatment was repeated two or three times, until the substance was perfectly white and did not change color when washed with alcohol and ether. It was then dried for a short time over sulphuric acid and paraffine, and was analyzed with the following results:

I. 0.2410 gram substance gave on combustion 0.3459 gram CO_2 and 0.1064 gram H_2O.

II. 0.2005 gram substance gave 0.2943 gram CO_2 and 0.9720 gram H_2O.

III. 0.1920 gram substance gave 0.1851 gram AgCl (Carius).

IV. 0.2372 gram substance gave 0.2233 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2$.	Found. I.	II.	III.	IV.
Carbon	39.87	39.13	40.02		
Hydrogen	4.65	4.90	5.38		
Chlorine	23.59			23.83	23.28

These results indicate that the substance is a dimethoxydichlorquinone to which two molecules of methyl alcohol have been added. To confirm this view of its composition the sodium salt was prepared and analyzed as follows: An excess of the insoluble compound was added to a solution of sodic methylate in a large quantity of methyl alcohol. As the sodium salt formed is soluble in methyl alcohol,[1] while the original compound is not, it was easy by filtering to obtain a pure solution of the salt, from which it was then precipitated by adding an excess of ether. The precipitate was repeatedly washed with ether by decantation, transferred to a weighed platinum crucible, dried over sulphuric acid and paraffine, and analyzed with the following results:

I. 0.2372 gram salt gave 0.0828 gram Na_2SO_4.

II. 0.2887 gram salt gave 0.1025 gram Na_2SO_4.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$.	Found. I.	II.
Sodium	11.24	11.31	11.50

[1] In the preparation of the original substance the sodium salt was obtained as a precipitate, because the amount of methyl alcohol used was not enough to dissolve it.

As these analyses indicate that the salt contains two molecules of methyl alcohol of crystallization, an attempt was next made to determine the amount of volatile matter which it contained, with the following result:

0.3177 gram salt heated at 100° lost 0.0501 gram.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$.	Found.
Methyl Alcohol	15.65	15.77

Another sample of the sodium salt was then dried at 100° to a constant weight, and a sodium determination was made in the dry substance:

0.2422 gram salt gave 0.1018 gram Na_2SO_4.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2$.	Found.
Sodium.....	13.33	13.61

These results show that, by the action of sodic methylate upon the dichlordiphenoxyquinone in the first place the two phenoxy groups are replaced by two methoxy groups, and then two molecules of sodic methylate are added directly to the molecule of dichlordimethoxyquinone formed by the first part of the action. The proof that these two molecules of sodic methylate are attached to the carbonyl groups of the quinone has been given in the introduction to this paper, and the new substance therefore is dichlordimethoxyquinone dimethylhemiacetal.

Other Methods of Preparing the Dichlordimethoxyquinone Dimethylhemiacetal.

This body can be made also directly from chloranil by the action of sodic methylate. When one equivalent of chloranil was treated with five or six equivalents of sodic methylate dissolved in methyl alcohol, a green salt containing sodium separated. This salt was dissolved in water rendered alkaline by a little sodic hydrate, and the addition of a dilute acid to this solution produced a dirty-white precipitate, a portion of which was soluble in alcohol, while the rest remained undissolved. The insoluble part, after purification by dissolving in sodic hydrate and filtering, was precipitated again with dilute sulphuric acid, and washed with water and alcohol, after which it was dried in a desiccator, and the chlorine determined:

0.2060 gram substance gave 0.1962 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2$.	Found.
Chlorine.....	23.59	23.55

That this product was the same as that prepared from the dichlordiphenoxyquinone was shown also by its properties, which agreed with those observed for that substance, especially by its very characteristic reaction with dilute acids.

The other product obtained from the green salt formed by the action of sodic methylate on chloranil was dissolved in the alcohol used in washing the dirty-white precipitate from dilute sulphuric acid; after evaporating off the alcohol, it was purified by recrystallization from dilute alcohol, and analyzed with the following result:

0.2094 gram substance gave 0.4841 gram AgCl (Carius).

	Calculated for $C_6Cl_4(OH)_2$.	Found.
Chlorine.....	57.25	57.16

As it melts at 235°, there can be no doubt that it is the tetrachlorhydroquinone, the melting-point of which is given by Sutkowski[1] as 232°. We are unable to determine at present whether this tetrachlorhydroquinone is due to a secondary reaction, or whether it proceeds from that by which the hemiacetal is made. Sodic ethylate does not act in this way with chloranil.

The dichlordimethoxyquinone dimethylhemiacetal is also formed when dichlordimethoxquinone (melting at 141°–142°) is treated with two equivalents of sodic methylate dissolved in methyl alcohol.

Properties of the Dichlordimethoxyquinone Dimethylhemiacetal.—It is a white amorphous solid, insoluble in all the common solvents. It is very easily converted into the red dichlordimethoxyquinone, melting at 141°–142°, discovered by Kehrmann.[2] This change can be effected by heat alone, since in the neighborhood of 160° it begins to take on a slight reddish color, which becomes darker very slowly at this temperature, but when heated to 195° or higher, the substance melts to a red liquid, at the same time increasing very much in volume and giving off many bubbles of gas consisting probably of the

[1] Ber. d. chem. Ges., **19**, 2316.
[2] J. prakt. Chem., [2], **40**, 370.

vapor of methyl alcohol. The decomposition-point is not a definite one, as in different trials this action took place at temperatures sometimes as much as twenty or twenty-five degrees apart. An easier way to bring about this change is by treating the hemiacetal with dilute sulphuric acid or dilute hydrochloric acid, to either of which it shows itself remarkably susceptible, the decomposition taking place quantitatively, slowly in the cold, but quickly on warming. The ease with which it is attacked by dilute acids is its most striking property. Continued boiling with water or with dilute alcohol or glacial acetic acid brings about the same decomposition, as does also treatment of either the free substance or its sodium salt with benzoyl chloride in a sealed tube at 100°, methyl benzoate being the secondary product. Acetic anhydride decomposes it in the same way, but more slowly; on the other hand, neither methyl nor ethyl iodide acts on the sodium salt or the free substance. The formation of the benzoic ester of the substance is described below.

The hemiacetal is a weak acid, forming with sodic methylate the white crystalline sodium salt, the method of preparation and analysis of which have been given above. This salt is soluble in water or alcohol, insoluble in ether. With argentic nitrate a white non-crystalline silver salt is formed, which is insoluble in water, and easily decomposed.

Action of Sodic Ethylate on Dichlordiphenoxyquinone—Dichlordiethoxyquinone Diethylhemiacetal, $C_6Cl_2(OC_2H_5)_2(OH)_2(OC_2H_5)_2$.

In order to study this action 10 grams of dichlordiphenoxyquinone were treated with an alcoholic solution of little less than four equivalents of sodic ethylate, which was made by treating 2.5 grams of metallic sodium with 60 cc. of absolute alcohol. When the sodic ethylate was first added there was no apparent action but, on standing, even in the cold, the red color of the dichlordiphenoxyquinone gradually disappeared, and a white crystalline sodium salt was formed. After warming gently on the water-bath to finish the reaction, the solution was filtered, the salt washed with alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in

excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and then with water again. In order to purify the substance further, it was dissolved in dilute sodic hydrate, filtered, precipitated again with dilute sulphuric acid, and washed thoroughly, as above. This treatment was repeated until finally the substance was perfectly white, and did not change color when washed with alcohol and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results :

I. 0.2205 gram substance gave on combustion 0.3802 gram CO_2 and 0.1304 gram H_2O.

II. 0.2017 gram substance gave 0.1614 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OC_2H_5)_2O_2(C_2H_5OH)_2$.	Found. I.	II.
Carbon	47.06	47.02	....
Hydrogen	6.16	6.57	....
Chlorine	19.89	....	19.78

These results show that the action of the sodic ethylate on the dichlordiphenoxyquinone is analogous to that of sodic methylate, since two phenoxy groups are replaced by two ethoxy groups, and then two molecules of sodic ethylate are added directly to one molecule of the dichlordiethoxyquinone thus formed, giving the sodium salt of dichlordiethoxyquinone diethylhemiacetal. The yield of the sodium salt from 10 grams of dichlordiphenoxyquinone was usually a little less than 10 grams, and therefore, as the change from the sodium salt to the hemiacetal is nearly quantitative, we obtained over 75 per cent. of the theoretical yield.

Properties of the Dichlordiethoxyquinone Diethylhemiacetal.—It is a white amorphous solid, which dissolves slightly in alcohol, but is partially decomposed by this solvent, so that it cannot be recrystallized from it. It is essentially insoluble in all the other common solvents. By boiling with dilute sulphuric or hydrochloric acid it is decomposed, and the same reaction takes place more slowly when it stands with the dilute acid in the cold. The product of the action in either case is a light red body melting at 104°–105°, after being purified by crystallization from alcohol, which is, therefore, dichlordiethoxyquinone, as this is the melting-point ascribed to

this substance by Kehrmann.[1] Stenhouse,[2] who discovered it, gives its melting-point as 107°; but even by repeated recrystallization we have not been able to raise the melting-point above 104°–105°, and therefore have come to the conclusion that Stenhouse's higher number must be due to an error. The white insoluble hemiacetal melts at 140°–143°, or rather decomposes at this temperature, changing into the red dichlordiethoxyquinone, which then melts. From these properties it appears that the relationship between the diethyl and dimethylhemiacetals is of the closest sort.

Like the corresponding methyl compound the dichlordiethoxyquinone diethylhemiacetal has acid properties, forming with sodic hydrate a sodium salt. It shows toward sodic hydrate a stability in marked contrast to its susceptibility to the action of dilute acids, as it is necessary to boil it with a strong solution of sodic hydrate in order to saponify it to chloranilic acid. The sodium salt of the diethylhemiacetal is white and crystalline, readily soluble in water, slightly soluble in alcohol, and insoluble in ether. The dried salt is slowly decomposed on standing in a closed bottle for several weeks, alcohol is given off, and a solid product left which contains some sodic chloranilate and another body, or more than one, which we have not yet identified. The silver salt is insoluble, and has a slight brownish-yellow color. It is blackened by light, alcohol being set free. On warming with water a red substance is formed, probably chloranilic acid. Insoluble salts were also obtained with solutions containing barium, calcium, lead, or zinc, but they were not studied. The details of the preparation of the sodium and silver salts will be found under the preparation of dichlordiethoxyquinone tetraethylacetal, later in this paper.

Dichlordimethoxyquinone Diethylhemiacetal,

$C_6Cl_2(OCH_3)_2(OH)_2(OC_2H_5)_2$.

This substance was made by treating 0.9 gram of dichlordimethoxyquinone with an alcoholic solution of sodic ethylate made from 0.2 gram of metallic sodium and absolute alcohol. After warming the mixture for a few minutes, all the red

[1] J. prakt. Chem., [2], **40**, 365. [2] Ann. Chem. (Liebig), Suppl., **8**, 14.

dichlordimethoxyquinone disappeared, and a crystalline sodium salt was deposited. The liquid was then cooled, the precipitate filtered out, washed with a little alcohol, and dissolved in water, in which it is completely and easily soluble. The aqueous liquid after filtration was treated with dilute sulphuric acid, which threw down a white bulky precipitate of the free hemiacetal, and this, after thorough washing with water, alcohol, and ether, was dried over sulphuric acid and paraffine, and analyzed with the following result:

0.1892 gram substance gave 0.1627 gram AgCl (Carius).

	Calculated for $C_6Cl_2(OCH_3)_2(OH)_2(OC_4H_9)_2$.	Found.
Chlorine	21.58	21.26

The dichlordimethoxyquinone diethylhemiacetal, like those hemiacetals which have been described already, is an amorphous white solid, essentially insoluble in all the common solvents. It is decomposed at temperatures between 140° and 160°, forming a red substance, probably dichlordimethoxyquinone, and it is easily saponified by dilute acids.

[*To be continued.*]

FROM PINENE TO CARVACROL.

By John L. Mead and Edward Kremers.

The conversion of pinene into pinene nitrosochloride and of the latter into the so-called "nitrosopinene," is generally known. That the last mentioned compound has been misnamed, that it is not a nitroso derivative but an oxime, was demonstrated by Mr. Urban and one of us a year ago.[1] Although the abstract in the *Berichte*,[2] concluded with the sentence "Die Untersuchung des Oeles, vermuthlich eines Ketones, $C_{10}H_{14}O$, ist in Angriff genommen," Prof. A. v. Baeyer[3] saw fit to ignore the work already accomplished, and to publish the results of some of his own investigations on the same subject. That the product of hydrolysis of the oxime[4] $C_{10}H_{14}NOH$ is not a ketone but a phenol, was recognized shortly after the publication of the note already referred to,

[1] This Journal, **16**, 404. [2] Referate, **27**, 793.
[3] Ber. d. chem. Ges., **28**, 646.
[4] v. Baeyer supposes it to be a binitrosyl derivative.—*loc. cit.*

and as soon as sufficient material for experimentation had been prepared. That this phenol is carvacrol Prof. v. Baeyer has already stated, basing his conclusion upon a single reaction. Inasmuch as this conversion of nitrosopinene into carvacrol appeared to be of great importance, it was thought best not to be content with a single proof, but to obtain sufficient evidence to establish the identity of the resulting product, beyond all reasonable doubt. This had been accomplished before Prof. v. Baeyer's publication.

Hydrolysis of so-called Nitrosopinene.—The nitrosopinene is dissolved in concentrated hydrochloric acid and after solution has been effected, about one-half the quantity of water is added. The solution is then heated on a water-bath until the reaction, which is rather violent at first, is ended. The oil which separates is distilled with water-vapor, a small quantity of black resin remaining behind. The presence of hydroxylamine was easily ascertained. The yield was about 65 per cent.

The oily distillate, which was of a light reddish color, was dried with anhydrous copper sulphate and fractionated. More than 75 per cent. distilled within 2°, *viz.*, 230–232°. Most of this fraction distilled at 231.5° uncorr., or 236.7 corr., under a barometric pressure of 743 mm. A redetermination of the boiling-point of this fraction, under a pressure of 725 mm., gave 230.3° uncorr. and 235.6° corr., respectively.

The rectified oil was of a light yellow color and possessed a decided phenol odor. Its density at 20° was 0.9780. It was optically inactive. Its index of refraction was found to be $N = 1.52128$, hence the coefficient of refraction $R_n = \frac{N^2-1}{(N^2+2)d} = 0.31151+$.

Attempts to crystallize the oil at ordinary temperatures failed. When exposed to a temperature below —100°, it formed a transparent amorphous solid. Upon rise of temperature the mass softened at about —40°, crystallized at from —20° to —18°, and melted at —0.5°.

Upon analysis the following results were obtained:

I. 0.2686 gram phenol yielded 0.7709 gram $CO_2 = 0.21024$ gram C, and 0.2359 gram $H_2O = 0.02621$ gram H.

II. 0.2733 gram phenol yielded 0.7853 gram CO_2 = 0.21417 gram C, and 0.2402 gram H_2O = 0.02668 gram H.

	Calculated for $C_{10}H_{14}O$.	Found. I.	Found. II.
C	80.00	78.27	78.36
H	9.33	9.76	9.40
O	10.66		

The phenol is but sparingly soluble in water, but freely soluble in alcohol, ether, chloroform, etc. It is also soluble in solutions of the fixed alkalies of more than 2 per cent. strength, from which solutions it is precipitated upon the addition of acids.

Its aqueous solution is colored green by ferric chloride, and from this solution small crystals separate in the course of time, which melt at 145°–147°. The oil heated with chloroform and caustic alkali, produces a crimson color fading to brown.

The transparent, prismatic crystals of the sulphonic acid melted at 57°–58°. The barium and lead salts were prepared, and quantitative determinations of the metals and of water of crystallization were made. The results will be given in the table below.

From the sulphonic acid the nitro compound was also prepared. The clear, dried crystals melted at 114°–116°. The melting-point remained practically unchanged upon recrystallization from hot petroleum-ether. Nitrogen determinations were made with the following results:

I. 0.3900 gram substance yielded 41.3 cc. gas at 23° and 736 mm. pressure = 0.04628 gram N = 11.87 per cent.

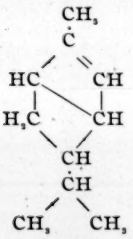
II. 0.5204 gram substance yielded 54 cc. gas at 20° and 742 mm. pressure = 0.0615 gram N = 11.83 per cent.

Dinitrocarvacrol, $C_{10}H_{11}(OH)(NO_2)_2$, contains 11.66 per cent. nitrogen.

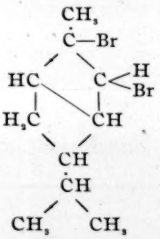
With bromine and iodine no crystalline substitution-products were obtained. These negative results as well as the positive results enumerated indicate beyond doubt that the phenol in question is *carvacrol* and not thymol, its isomer.

	Thymol.	Phenol from Pinene.	Carvacrol.
Boiling-point	228°–230°	235.6°	236°–237°
Melting-point	50°	—0.5°	0°
d	0.9689 at 24½°	0.9780 at 20°	0.9752 at 20°
N	——	1.52128	1.52344
R	0.31300	0.31151	0.31200
Melting-point of sulphonic acid	98°	57°–58°	65°
Melting-point of dinitro compound	55°–56°	115°	117°
	Per cent.	Per cent.	Per cent.
Percentage Ba in Ba-salt	20.5	20.10	19.97
Water of crystallization of Pb-salt	9.74	12.19	11.90
Percentage Pb in Pb-salt	28.00	27.60	27.34

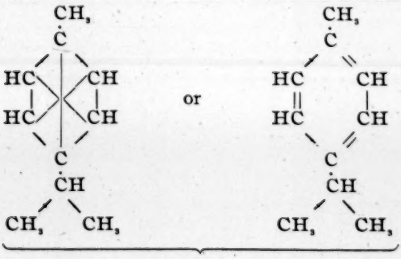
Wallach[1] has explained the formation of cymene from pinene dibromide, with the aid of the following formulas:



Pinene.



Pinenedibromide.

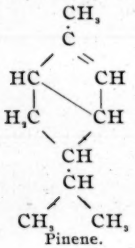


Cymene.

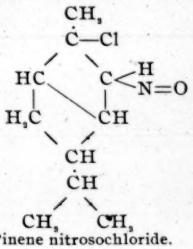
Being guided by the course of the reactions, which take place in the conversion of menthene to Δ^4 terpene-3-one,[2]

[1] Ann. Chem. (Liebig), 268, 213. [2] Proc. Am. Pharm. Assoc., 43,270.

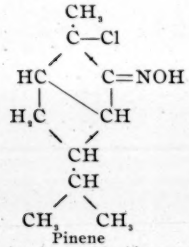
the conversion of pinene into carvacrol can be explained satisfactorily with the aid of Wallach's pinene formula—



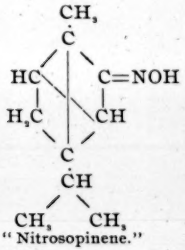
Pinene.



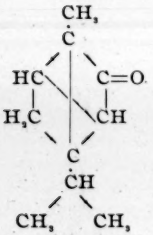
Pinene nitrosochloride.



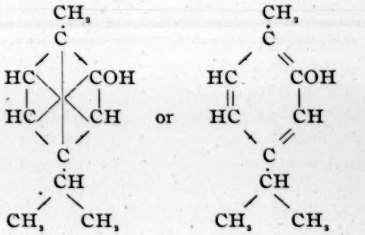
Pinene isonitrosochloride.



"Nitrosopinene."



Ketone from "Nitrosopinene." Intermediate product of hydrolysis.



Carvacrol, final product of hydrolysis.

PHARMACEUTICAL CHEMICAL LABORATORY,
UNIVERSITY OF WISCONSIN.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON HALOGEN ADDITION-PRODUCTS OF THE ANILIDES.

[*Preliminary paper.*]

BY H. L. WHEELER.

This paper contains a description of the bromination of metanitroacetanilide. In this case I have succeeded in isolating a comparatively stable dibrom addition-compound, which is the first substance formed when bromine is added to the anilide. From this addition-compound the so-called substitution-product is then obtained by the separation of hydrobromic acid. This is the first halogen addition-product that has been obtained in the case of the anilides.

Experiments are now in progress in this laboratory which show that analogous halogen addition-products can be prepared from other anilides. A description of these will be given in a later paper. This preliminary notice, in the case of metanitroacetanilide, is given in order that I may reserve the field for myself.

These addition-products are especially interesting since they show that the process which is usually called substitution, in the case of the anilides, is really addition, then a separation of halogen hydride with the consequent formation of the so-called substitution-product.

Action of Bromine on Metanitroacetanilide.

When bromine is mixed with dry metanitroacetanilide the substances combine with evolution of heat but without giving off hydrobromic acid. When this mixture is strongly heated it melts with effervescence and torrents of hydrobromic acid are evolved. On cooling, if it has been carefully heated, the residue solidifies to a light yellow mass; this, on crystallizing once from benzene, gives pure parabrommetanitroacetanilide, melting at 143°. The base obtained from this by removing the acetyl group melts at 131°. If, on the other hand, the mixture is treated with sulphurous acid or ammonia, the halogen is quantitatively removed and metanitroacetanilide is recovered. Thus obtained, the anilide melts at 152° and the base at 114°.

These facts led the author to attempt the isolation of the bromine addition-product that is evidently formed here. The best results were obtained in the following manner: Metanitroacetanilide was dissolved in nitrobenzene, in which it is readily soluble, an excess of bromine was added, and the clear solution was then precipitated with dry ligroïn: a heavy translucent dark-red oil separated. The whole was transferred to a separatory funnel and the supernatant ligroïn solution, containing the nitrobenzene and excess of bromine, decanted. The oil was then shaken thoroughly three times, each time with over its own volume of dry ligroïn. A portion was then taken out by means of a pipette and immediately corked in a weighing-tube. After weighing the substance, the tube was uncorked and plunged into dilute ammonia. A bromine determination was then made in the usual way. [Analysis I.] The remaining portion of the oil was then shaken again with more ligroïn. It began to crystallize. A portion was removed and a bromine determination made. [Analysis II.] After shaking what remained again, the fifth time, with more ligroïn, considerable material separated in the solid condition. On exposing a portion of this oil to the air it immediately solidified. The material was separated as before and analyzed. [Analysis III.]

I. 0.6392 gram substance gave 0.6922 gram AgBr.

II. 0.4270 gram substance gave 0.4670 gram AgBr.

III. 0.5067 gram substance gave 0.5565 gram AgBr.

	Found.			Calculated for $C_8H_8N_2O_3.Br_2$.
	I.	II.	III.	
Br	46.1	46.5	46.7	47.0

In dry chloroform or glacial acetic acid containing bromine, the addition-product remains unaltered for days. It can be crystallized from these solvents. It then separates in the form of radiating bunches of flattened, transparent, bright yellow prisms. These melt with effervescence at 143°. The addition-product therefore has the same melting-point as the substitution-product. A specimen crystallized from glacial acetic acid containing bromine and rapidly pressed on paper, was then placed in a tightly corked weighing-tube for analysis.

0.3221 gram substance gave 0.3415 gram AgBr.

	Found.	Calculated for $C_8H_8N_2O_3.Br_2$.
Br	45.1	47.0

Specimens were obtained by preparing a hot saturated chloroform-solution of metanitroacetanilide, adding an excess of bromine and then allowing the whole to cool. An excess of bromine must be present, otherwise the unaltered anilide separates along with the addition-product. A crystalline product thus obtained was rapidly pressed on paper and dried on the water-bath. [Analysis I.] Another portion of the same was dried by exposing it for a short time to the air. [Analysis II.] A third portion was rapidly pressed on paper, and, in order to avoid decomposition by exposure, the material, which was still slightly moist with the mother-liquor, was immediately analyzed. [Analysis III.]

I. 0.3200 gram substance gave 0.3330 gram AgBr.

II. 0.2200 gram substance gave 0.2232 gram AgBr.

III. 0.3498 gram substance gave 0.3952 gram AgBr.

	Found.			Calculated for
	I.	II.	III.	$C_8H_8N_2O_3.Br_2$.
Br	44.3	43.2	48.0	47.0

These analyses show that the substance is a dibrom addition-product. The low results are due to the fact that some bromine is lost in the process of drying. When the addition-product is exposed to the air it gives off bromine. A portion exposed for twenty-four hours in a desiccator over potash and sulphuric acid, contained only 37.4 per cent. of the halogen. The residue in the case of a specimen exposed in this manner for a week consisted of a mixture of substances, apparently metanitroacetanilide, parabrommetanitroacetanilide, and the hydrobromic acid addition-products of these (see below).

Hydrobromic acid is liberated from the addition-product, with consequent formation of parabrommetanitroacetanilide, on heating or on crystallizing it from water. Water removes hydrobromic acid in the cold. Metanitroacetanilide and bromine, in the proportion to form the dibrom addition-product, were mixed under water. The material was then immediately filtered and converted into the base as indicated below. On crystallizing this base from water it was found to

be pure parabrommetanitraniline. This amounted to 64 per cent. of the calculated yield.

Cold concentrated nitric or sulphuric acid also separates hydrobromic acid from the addition-product. In these cases, however, the reaction takes place chiefly with displacement of bromine. A well crystallized specimen of the addition-product, obtained from a hot chloroform solution, was rapidly dried on the water-bath. On dissolving this in sulphuric acid drops of bromine sank to the bottom of the solution and fumes of hydrobromic acid escaped. The bromine was removed by means of a stream of air and the solution poured into ice-water. The substance that separated was crystallized from water, when yellowish white tables were obtained. These melted at 152° (not sharply). This material was, therefore, chiefly metanitroacetanilide; it, however, contained some parabrommetanitroacetanilide, as shown by qualitative tests for bromine.

Metanitroacetanilide is recovered from the addition-product and the bromine is quantitatively removed by means of the alkalies, ammonia, or sulphurous acid. Moist silver oxide also removes bromine. Metanitroacetanilide is also obtained when the addition-product is crystallized from strong alcohol. These reactions preclude the possibility that, in the formation of parabrommetanitroacetanilide, substitution first takes place and that the resulting hydrobromic acid remains combined with the anilide.

Parabrommetanitroacetanilide.—This compound was best prepared by treating the dibrom addition-product with water. When the substance thus treated was crystallized from hot water, it separated in the form of pale yellow needles or prisms. For analysis the material was dried at 100° and a bromine determination made according to the method of Carius:

0.2040 gram substance gave 0.1452 gram AgBr.

	Found.	Calculated for $C_8H_7N_4O_3Br$.
Br	30.3	30.8

If in the preparation of this compound an excess of bromine is employed and the whole warmed for some time, the acetyl

group is removed, and then *s*-tribrommetanitraniline is formed.

Parabrommetanitraniline (NH_2,NO_2,Br : 1, 3, 4).—This results when the above acetyl compound is boiled for a few minutes with alcohol and concentrated hydrochloric acid. On evaporating the alcohol and adding ammonia the base is precipitated. This, on crystallizing from hot water, gives very long, bright yellow slender needles, melting at 131°. This base is identical with the compound obtained by nitrating parabromaniline according to the method of Nölting and Collin.[1] A specimen thus obtained was converted into the acetyl compound. This melted at 143° and had the same properties as the compound obtained from the addition-product. The structure of the base obtained from the acetyl compound was confirmed by converting it into dibromnitrobenzene (NO_2,Br,Br : 1, 2, 5), according to Sandmeyer's[2] method. This base differs little in basicity from metanitraniline. Salts can readily be prepared by the usual methods. These are decomposed by water.

The *hydrochloride*, $C_6H_3.N_2O_2Br.HCl$, crystallizes in extremely long, slender, colorless needles.

0.3131 gram substance gave 0.1763 gram AgCl.

	Found.	Calculated for $C_6H_3.N_2O_2Br.HCl$
HCl	14.3	14.4

The *sulphate*, $(C_6H_3.N_2O_2Br)_2.H_2SO_4$, crystallizes in long, slender, colorless needles. With only a few grams of material crystals over 5 cm. in length were obtained.

0.3282 gram substance gave 0.1410 gram $BaSO_4$.

	Found.	Calculated for $(C_6H_3.N_2O_2Br)_2.H_2SO_4$
H_2SO_4	18.0	18.4

Theoretical Considerations.

No derivatives of the dibrom addition-product of metanitroacetanilide have yet been prepared, but the evidence thus far obtained in regard to its structure, indicates that the halogen adds itself to the benzene nucleus and not to the nitrogen of the anilide group. If it be assumed that the bromine adds itself to the nitrogen of the anilide group, the addition-product

[1] Ber. d. chem. Ges., 17, 266.
[2] *Ibid.* 17, 2652.

would then be a derivative of pentavalent nitrogen (I.) or, less probably, of the pseudo form of the anilide (II.)

I. II.

$RNBr\boxed{BrH}.COCH_3$. $RNBr.C\boxed{Br}O\boxed{H}CH_3$.

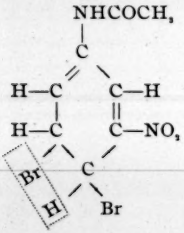
In the formation of the substitution-product from such compounds it would be expected that hydrobromic acid would separate from the anilide group as indicated by the dotted lines. The resulting compound, $R.NBrCOCH_3$, would then, by a molecular rearrangement give parabrommetanitroacetanilide, being an analogue of Bender's[1] chloracetanilide, $C_6H_4.NClCOCH_3$, which readily undergoes this rearrangement. This however is not the case. Hydrobromic acid separates in a different manner. This is shown by the fact that bromine addition-products can be prepared from methylmetanitroacetanilide, $C_6H_4.NO_2.NCH_3COCH_3$, and the dibrom derivative formed in this case readily separates hydrobromic acid. Here the possibility of such a separation of hydrobromic acid as indicated above is excluded. Therefore, on the assumption that the bromine combines with the nitrogen, it is not evident in what manner the substitution-product is formed.

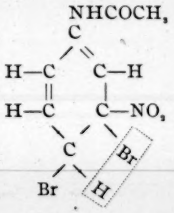
On the other hand the formation of the substitution-product is readily explained if it is assumed that the bromine adds itself to the benzene nucleus. Moreover the latter assumption is rendered exceedingly probable by the fact that metanitroacetanilide combines with more than two atoms of bromine. This is shown by the following: When metanitroacetanilide is mixed with bromine in the proportion of one molecule of the anilide to four atoms of bromine, the substances combine with evolution of enough heat to effect the liquefaction of the mixture. This soon commences to solidify, and in a few minutes becomes a hard, reddish-colored, perfectly solid mass which can be pulverized and taken in the hand without injury to the skin. The bromine evidently combines with the anilide to form, presumably, a tetrabrom addition-product.

The formation of this higher bromine addition-product was frequently observed when a hot chloroform-solution of metanitroacetanilide was treated with a large excess of bromine.

[1] Ber. d. chem. Ges., 19, 2272.

It then separated along with the dibrom compound, imparting to the latter a deep red color. It is extremely unstable. When it is removed from the mother-liquor it immediately evolves bromine, in the form of vapor, decomposing rapidly into the bright yellow di-derivative. Various specimens obtained in this manner and pressed on paper until they gave no stain, gave analytical results showing that the substance contained bromine in excess of that calculated for the dibrom addition-product. These results varied from 48.0 to 56.8 per cent., of bromine. The calculated amounts of bromine in the dibrom and tetrabrom addition-products are 47.0 and 64.0 per cent., respectively. On account of the unstable nature of this higher addition-product, further attempts to isolate it were abandoned. These facts show however, that metanitroacetanilide combines with more than two atoms of bromine. It therefore seems probable that the unsaturated affinities between the carbon atoms of the benzene nucleus are the points where addition takes place, and that the bromine does not unite with the nitrogen of the amido group. Assuming Kekulé's formula for the benzene nucleus the structure of the dibrom addition-product would then be represented by either of the two following formulas:





The dotted lines indicate the manner in which parabrommetanitroacetanilide then results by separation of hydrobromic acid. It is hoped that by a wider study of the halogen addition-products of the anilides further evidence in regard to their structure may be obtained.

Attempts were made to prepare the dibrom addition-product

by reversing the above operation and adding hydrobromic acid to parabrommetanitroacetanilide. Hydrobromic acid addition-products were readily obtained but these belonged to entirely different types. An isomeric addition-product, which probably has the structure of an ammonium salt, was obtained when 0.5 gram of parabrommetanitroacetanilide was dissolved in 20 cc. of a mixture of glacial acetic acid and ethyl acetate, and the solution saturated with dry hydrobromic acid gas. This compound separated in the form of beautiful colorless needles. Ammonia removed only one bromine atom in the form of hydrobromic acid. For analysis the substance was rapidly dried as far as possible by pressing on paper.

0.1662 gram substance gave 0.0882 gram AgBr.

	Found.	Calculated for $C_8H_7N_3O_5Br.HBr$.
HBr	22.8	23.8

The formation of another hydrobromic acid addition-product was observed when 3 grams of parabrommetanitroacetanilide were dissolved in glacial acetic acid and hydrobromic acid gas was passed into the solution for a short time. Colorless crystals, apparently rhombohedrons, separated. These were dried on paper.

0.2415 gram substance gave 0.0887 gram AgBr.

	Found.	Calculated for $(C_8H_7N_3O_5Br)_2HBr$.
HBr	15.8	15.6

These addition-products lose hydrobromic acid on exposure to the air. A specimen of the latter exposed for twenty-four hours contained 14.0 per cent. of hydrobromic acid.

It is noteworthy that when the higher bromine addition-products of metanitroacetanilide are heated or crystallized from water, not more than one molecule of hydrobromic acid separates from the acetyl compound. Hence all attempts to prepare a higher substitution-product than parabrommetanitroacetanilide were without success. A search was also made for isomeric monobrom derivatives that might be formed. No trace of these could be detected.

Contributions from the Chemical Laboratories of the Massachusetts Institute of Technology.

XIII.—SYNTHESIS OF DIPHENYLBIPHENYL AND ITS IDENTIFICATION AS BENZERYTHRENE.

By Arthur A. Noyes and Rolfe M. Ellis.

The purpose of this investigation was to prepare synthetically the compound diphenylbiphenyl, $C_6H_5.C_6H_4.C_6H_4.C_6H_5$, and to determine by a comparison of its properties, whether, as might be expected, it is one of the products of the action of heat on benzene. It seemed probable that this substance might be obtained by the Fittig reaction, by the treatment of brombiphenyl with sodium, and accordingly, an attempt was made to prepare it in this way.

Biphenyl was made in the usual manner, by passing benzene through a red-hot tube. From this, brombiphenyl was prepared as described by Schultz.[1] It is to be noted that the body thus obtained is the para compound, since it yields parabrombenzoic acid on oxidation.[2]

30 grams of brombiphenyl were dissolved in three to four times that quantity of absolute ether, and an excess (5 grams) of thin cut sodium added. The mixture soon heated to boiling, too violent action being prevented by surrounding the vessel with cold water. After two or three days the insoluble residue was separated from the ethereal solution by filtration. The solution was found to contain only unchanged brombiphenyl, and was used as the solvent for the brombiphenyl in the next sodium treatment. The residue was repeatedly extracted with hot water to remove the sodium bromide and excess of sodium. It was then dried and treated with successive quantities of cold benzene, (200 cc. in all), which dissolved much the larger portion. By the addition of alcohol to this benzene solution, there was precipitated a brown flocculent substance insoluble in ether, chloroform, and petroleum-ether, but very soluble in benzene and carbon bisulphide. All attempts to purify it by crystallization, subli-

[1] Ann. Chem. (Liebig), **174**, 207.
[2] *Ibid.* **174**, 209.

mation, and distillation failed. The residue insoluble in benzene was of a dirty white color. It was found to sublime at a high temperature, and was purified between watch-glasses in this manner.

The sublimate was pure white, and in the form of large crystalline leaflets. It was proved to be pure diphenylbiphenyl by combustion and by a vapor-density determination, made by the Victor Meyer method, in the vapor of boiling phosphorus pentachloride, (520°).

0.1364 gram substance gave 0.4684 gram CO_2 and 0.0735 gram H_2O.

0.1404 gram substance gave 11.70 cc. air, measured over water at 27° and 759 mm.

	Calculated for $C_{24}H_{18}$.	Found.
C	94.12	93.65
H	5.88	5.99
Vapor-density	10.64	10.57

From the constitution of the brombiphenyl used, it follows that the phenyl groups occupy the para positions with respect to the central bond.

The yield obtained was in all cases very small, amounting to only five per cent. of the theoretical.

Several attempts were also made to prepare the body by the action of sodium on brombiphenyl in boiling benzene solution, but entirely without success. The product consisted wholly of the brown flocculent substance referred to above, as precipitated by alcohol from the benzene extract.

The melting-point was accurately determined by heating portions of the substance enclosed in sealed capillary tubes, in a flask in the vapor of boiling diphenylamine, the external pressure, and consequently the boiling-point, being gradually increased until the substance liquefied. The temperature was then noted by means of a tested thermometer wholly immersed in the vapor. The melting-point was found to be 317°.

The substance distilled without decomposition under a pressure of 18 mm. at 428° (roughly determined with a mercu-

rial thermometer). Its behavior during the heating in the vapor-density determination, showed that its boiling-point under ordinary pressure is below 520°, and that it is stable at that temperature.

The substance is completely insoluble in boiling alcohol, ether, chloroform, and carbon bisulphide, and in cold benzene. It was but slightly soluble in boiling benzene, one part requiring more than one hundred parts of the solvent.

It is of interest to compare these properties with those of the isomeric substance, *s*-triphenylbenzene, which has been previously prepared by various investigators. The latter substance boils at 459° at 717 mm. (Crafts), melts at 170°, and is soluble in benzene.

It now remains to determine whether diphenylbiphenyl is produced by the action of heat on benzene. It is evident that it might result from a condensation of biphenyl in a manner similar to that by which this substance is formed from benzene.

A most thorough study of the high boiling hydrocarbons thus formed from benzene has been made by Schmidt and Schultz.[1] Of these, the one which they named benzerythrene agrees closely in properties with our hydrocarbon; for the analysis of it corresponded to the formula $C_{24}H_{18}$; it melted at 308°, boiled far above 360°, was insoluble in alcohol, and slightly soluble in boiling benzene, from which it crystallized on cooling. There is therefore, no doubt that the two substances are identical, and consequently that paradiphenylbiphenyl is produced by the action of heat on benzene. It seems probable that this substance might be obtained in considerable quantity by passing biphenyl through a red-hot tube.

REVIEWS.

Cellulose: An Outline of the Chemistry of the Structural Elements of Plants with Reference to their Natural History and Industrial Uses. By C. F. Cross and E. J. Bevan. London and New York: Longmans, Green & Co., 1895. 310 pp., 14 plates.

This work will prove a revelation even to those who are more or less familiar with the subject. It removes cellulose

[1] Ann. Chem. (Liebig), 203, 118.

from the position of an indefinite and loosely characterized substance, to that of a definite chemical body with characteristic reactions, and even offers some very clever theories as to its constitution. The authors have skillfully compiled the important features of the present knowledge of the subject, avoiding the repetition of much that is trite, and to this have added an account of their own extensive investigations. The treatise is a thoroughly scientific one, but embodying many practical ideas and frequently pointing out possible applications of the results of investigations to some of the many industries based upon cellulose and vegetable fibres. Indeed, nearly one-third of the book is devoted to a discussion of the experimental and applied phases of the subject.

At the outset the authors differentiate sharply between cellulose and much that goes by that name. Plant fibres are not necessarily composed of the typical cellulose, as is shown by their characteristic reactions. In general such materials are divided into two broad classes: the true celluloses, typified by cotton-fibre, and the compound celluloses of which the most important representatives are the lignified plant tissues or fibres, jute-fibre being studied as the type.

Cellulose proper possesses definite composition: carbon, 44.2 per cent.; hydrogen, 6.3 per cent.; and oxygen, 45.9 per cent.; corresponding to the formula $C_6H_{10}O_5$. It presents characteristic hydration-phenomena, and exists in the plant in all stages of hydration, varying in general with age. It is soluble in a variety of reagents, from which it may often be precipitated without essential change. This solution is regarded as being due to the formation of compounds of the nature of salts, between the solvents and the hydroxyl groups of opposite character in the cellulose molecule. In its capacity of a polyhydroxy body, cellulose forms several compounds with dilute acids and alkalies. As a derivative of one of these compounds, the alkali cellulose xanthate, discovered by the authors and described by them elsewhere, is one of the most important. Other definite compounds are the acetates, benzoates and nitrates, all of the nature of esters or ethers, and indicating the existence of hydroxyl groups in the molecule. Cellulose also forms with sulphuric acid a series of compounds of great variety and complexity. The cellulose molecule is decomposed by hydrolytic agents, by oxidation, by ferments, and by destructive distillation. No direct synthesis of cellulose has been accomplished or seems likely to be, but attention is called to the formation of cellulose from bodies of simpler molecular structure in the case of the ropy fermentation of beet-juice and the similar product of the vinegar ferment. Based upon these studies, the authors present their

conclusions in which they regard cellulose as an anhydro aggregate of dextrose or aldose molecules, $C_6H_{12}O_6$. In this aggregate the carbonyl groups are suppressed, and may be set free by the action of acids (hydrolysis). Resolution by fusion with alkalies into ultimate products of which acetic acid amounts to about 30 per cent., indicates that the grouping $CO.CH_3$ is an important one. The negative or indifferent characteristics of cellulose show it to be a saturated compound. Synthetical reactions such as the formation of acetates, nitrates and benzoates, indicate four hydroxyl groups in the original unit molecule $C_6H_{10}O_5$, capable of reacting without disturbing the original configuration. The authors are inclined to think that the arrangement of the carbon atoms is a cyclic one, pointing out the significance of the fact that so many bodies of this class are derived either directly or indirectly from fibre or cellulose-like materials.

Compound celluloses are modifications of the true celluloses in which the latter have been subjected to the action of lignification, suberisation, or conversion into mucilage. There are many forms of such compounds of which the most common and important is the ligno-cellulose typified by the fibre-substance of jute. The authors find this fibre-substance to be a compound and not an encrusted cellulose. It is capable of being decomposed into several groups of characteristic bodies, an outline of which is best shown as follows:

Ligno-cellulose.			
Cellulose.		Lignone (non-cell.)	
Cellulose α Containing oxidised groups.	Cellulose β Containing $O.CH_3$ groups.	Furfural-yielding complex and secondary constituents: $O.CH_3$ groups and CH_2CO residues.	Keto-R-Hexene groups

The ligno-celluloses are characterized by a higher percentage of oxygen than the true celluloses, with the properties of an unsaturated compound containing C_6-rings of a ketone or quinone character. Of the ligno-celluloses, two important reactions are discussed in detail, *viz.*, the reaction with chlorine, and the formation of furfural. These reactions are given by one or the other of the complexes above referred to. The chlorine reaction is apparently a direct addition of the halogen, producing a compound of definite composition. The reaction occurs with that portion of the ligno-cellulose commonly designated as lignin, and seems to be identical with the action of chlorine upon a quinone. Other constituents of the compound celluloses yield, upon distillation with strong hydrochloric acid, furfural. The authors conclude that two such constituents are capable of this change without definite-

ly pointing out their relation. One of these is the pentosan group and the other an oxycellulose group, without any apparent relations to the pentoses. It is significant however that, wherever the furfural reaction has been used as an indicator, and has been given with sufficient distinctness to warrant further investigation, it has been possible to prepare and isolate from the material appreciable quantities of the pentose sugars. There is doubtless some connection not yet well understood between all of the constituents of the compound colluloses which yield furfural.

The authors' theory of the origin and relation of the different kinds of cellulose is, that the true cellulose is an aggregation of simple carbohydrate molecules, that the so-called processes of lignification, etc., are really degrees of oxidation by which the molecular equilibrium of the true cellulose is disturbed. The resulting oxycelluloses are unstable, and tend to form closed-ring derivatives (furfural, lignone, keto-R-hexene bodies). The cellulose on the one hand, and the cyclic derivatives on the other, are connected by intermediate products which may be converted into cellulose-like bodies, into substances of low molecular weight, or into closed-ring compounds. There is in lignification a constant tendency toward cyclic compounds, in evidence of which the authors repeatedly refer to the secretion of aromatic derivatives and the formation of such products by destructive distillation of coal or wood. It is also pointed out in an interesting way, that cellulose is a non-nitrogenous excreted substance, and, so far as the plant is concerned, dead material.

The work is upon advanced ground and presents enough of fact and experimental data, to warrant the wholly plausible theories offered. To say that the latter will prove infallible is too much. The authors have, however, contributed the most valuable work upon the important subject of cellulose and plant fibres, in existence; a work which will serve as a valuable reference-book for a long time. In the light of so much that is excellent, it is out of place to call attention to minor criticisms, of which, indeed, few are to be found.

The paper upon which the book is printed, deserves special notice, being made from "normal" cellulose of enduring quality. W. E. STONE.

HANDBUCH DER STEREOCHEMIE. Edited by DR. C. A. BISCHOFF, Professor of General Chemistry at the Riga Polytechnic, with the collaboration of DR. PAUL WALDEN, Professor of Physical and Analytical Chemistry. Two vols. With 250 wood cuts and the portraits of Pasteur, Le Bel, and van't Hoff. Frankfurt a. M.: H. Bechhold. Vol. II, pp. 449–1060+xvi. 1894.

The first volume of this work has been already noticed in

these pages.[1] The second volume maintains the essentially cyclopædic character of the book, of which the first 200 pages are occupied with a continuation of the systematic enumeration of the cases of geometrical isomerism, with full references to the literature. Inorganic compounds occurring in more than one modification are included here. Criticisms and references to the editor's own views are rare, and this part of the book is intended for reference rather than for reading. At the close of the book is a valuable appendix (pp. 833–1026), which brings the references up to the year 1894. In the intermediate division, which deals with the influence of space-relations in chemical reactions, the treatment becomes more characteristic and of more immediate interest. Here the editor becomes author, and the *Handbuch* merges into the *Lehrbuch* and becomes quite readable. The first chapter of this section deals with ring-formation. Stereochemistry has long since pointed out that the tendency to this form of linkage depends not only on the affinity of the atoms composing the ring, but on their number, and their relative positions prior to the closing of the ring; and here we have brought together for the first time interesting proofs that the nature of the atoms composing side-chains has an important influence. There follows an enumeration of all the known ring-systems, including inorganic rings. The configuration of benzene and hexamethylene is not discussed, references only being given, "because the question is not definitely settled." If this rule had been adhered to throughout, the book would have been much shorter, but we should have lost all reference to Prof. Bischoff's hypothesis of dynamic isomerism, which here begins to emerge from the haze which has hitherto enshrouded it. "According to the principle of the dynamical hypothesis, that one of two possible configurations results (*ceteris paribus*) in greater quantity, which allows the freest possible oscillation of the components of the molecule in the conditions of the experiment" (p. 777). Further, these oscillations are supposed to be rotations about the valence-axes. Followed out on suitable—presumably tetrahedral—models, these rotations are seen to result in some cases in "collisions," and reactions which cannot take place without a collision will not take place at all; hence, "abnormal reactions." For example, where we should expect to form only $RC(CH_3)_2-CR(CH_3)_2$ we get also $RC(CH_3)_2-CH_2-CR(CH_3)_2$ because this configuration allows more room for the oscillations of the

[1] See this Journal, **16**, 475.

methyl groups. But as the usual models are defective, in that they do not show the distance of the atoms apart, deductions drawn from their collisions will often be wrong, and the models must be altered in accordance with the results of experiment till their indications agree with the facts. Moreover the oscillations will be modified by change of temperature, and the valence-axes, about which the oscillations take place, are supposed by many chemists to vary in direction—though on this point the author's views are not stated.

It seems difficult to devise crucial tests for a hypothesis of such an accommodating nature, and this is perhaps the reason that it has received scant attention from stereochemists. Perhaps the most definite indication of the theory is that like groups require more space than unlike groups, because, their orbits being similar, they are more likely to collide; so that if in the above formulæ one or two methyl groups were replaced even by the larger phenyl group, the first configuration might alone result, the phenyls being too far from the central carbon atoms to collide with the methyls.

Further developments of the dynamic hypothesis appear also in the chapter devoted to the limits of general reactions: "It is often observed that when a reaction takes place involving the compounds at the beginning of a homologous series a by-product results; but when we use a member of the series possessing a certain complexity the proportion of the by-product increases, and, as we ascend the series, it predominates, becoming the main product" (p. 817). This phenomenon may be brought about by the interaction of groups appearing in the structural formula to be far apart in the molecule, but which must be supposed to be in reality near together.

The complete explanation of these abnormal reactions may be far distant, but it is evident that Prof. Bischoff has taken the first steps towards it by thus collecting and classifying them. That there is something "unsatisfying" in this part of the book cannot be denied; just as we think one phenomenon is about to be "explained" the subject is dropped and another is hurried into view. We have neither a simple statement of facts nor a systematic review of them in the light of a completed theory. But this is perhaps the fault rather of the present state of stereochemistry than of the author.

In fact, since the grand generalizations of Van 't Hoff and Le Bel, stereochemical theory has been rather an aspiration than a fulfillment. Facts have multiplied apace, and useful working-hypotheses have not been wanting, but when we leave the ground which those chemists have made classic, we

find no longer the coherence, the harmony, the unity which facts present when viewed in the light of a theory which has kept pace with them. If Prof. Bischoff finds himself at present unable to supply this theory he does the next best thing in making us feel the lack of it. To decline to assume a virtue when our science has it not, to show shortcomings as well as advances, hidden weakness in the midst of apparent strength—these must be accounted essential merits in a scientific author writing on his special subject.

Few chemists will fail to find this book helpfully suggestive, and those who are specially interested in its subject will find it indispensable. Its value would be enhanced if we could be assured that appendices would from time to time be issued bringing the references to the literature up to date.

It must be observed that the book is not free from the misspelling of English names so common in German chemical literature. Thus we have on p. 15, Tail for Tait; on p. 92, Bush and March for Burch and Marsh; and on p. 995, Eilvart for

EILOART.

ELEMENTS OF QUALITATIVE AND QUANTITATIVE ANALYSIS. By G. C. CALDWELL, B.S., PH.D., Professor of General and of Agricultural Chemistry in Cornell University. Third Edition, revised and enlarged. Philadelphia: P. Blakiston, Son & Co.

"In this work the author has brought together what has already been published, separately, in the 'Manual of Qualitative Chemical Analysis,' by himself and Dr. S. M. Babcock, and the 'Notes on Chemical Analysis' by himself alone; he has added thereto, much matter on qualitative analysis, all of Parts III. and IV. on quantitative analysis, and nearly all of Part V." (Extract from preface). The material of the work is arranged under five heads: Part I. treats of the "Processes of Analytical Chemistry and Some of the Products of Its Operations;" Part II. is a "Systematic Course of Qualitative Analysis;" Part III. is devoted to the "Operations of Quantitative Analysis;" Part IV. contains "Examples for Practice in Quantitative Analysis;" and Part V. is given up to "Miscellaneous Matter," such as lists of apparatus and reagents, special directions for the use of the former and the preparation of the latter, tables, etc.

This work is justly open to one criticism which applies equally well to nearly all the present-day "laboratory guides," namely, that it offers the student no practice or discipline in the methods of Physical Chemistry. The great educational value of these methods can scarcely be questioned, and they should not be ignored in any work which is offered the student for his guidance in the laboratory.

H. N. M.

THE ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY, AND BLOWPIPE ANALYSIS, from a Practical Standpoint, Including a Description of all Common or Useful Minerals, the Tests necessary for their Identification, the Recognition and Measurement of their Crystals, and a Concise Statement of their Uses in the Arts. By ALFRED J. MOSES, E.M., Ph.D., Adjunct Professor of Mineralogy, Columbia College, School of Mines; and CHARLES LATHROP PARSONS, B.S., Professor of General and Analytical Chemistry, New Hampshire College. New York: D. Van Nostrand Co.

Part I. treats of crystallography, one chapter being given to general principles, six chapters to the 6 Systems of crystallization, one to the measurement ofcrystal angles, and one to the clinographic projection of crystal figures. Part II., including chapters X–XIII., is devoted to blowpipe analysis. Part III., including chapters XIV–XXXI., treats of descriptive mineralogy, the arrangement of the species being according to what may be called the leading chemical constituent. Part IV., chapter XXXII., is made up of tables designed to facilitate the recognition of the commoner minerals, either by their physical properties or by their conduct before the blowpipe. The style of the work is to be commended for its clearness, and the treatment of the subject is adequate to the needs of the class of students for which the book was written. H. N. M.

OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN. Leipzig: W. Engelmann.

Attention was directed in this place over a year ago[1] to Ostwald's valuable series of reprints of classical papers taken from the literature of the exact sciences. Since that time several volumes have appeared which will be of general interest to the readers of this JOURNAL; the following especially because of their bearing upon important departments of physical chemistry:

No. 40. Zwei Abhandlungen ueber die Waerme: Lavoisier und Laplace—*M.* 1.20.

No. 42. Das Volumgesetz gasförmiger Verbindungen: Humboldt und Gay-Lussac—*M.* 0.60.

No. 44. Das Ausdehnungsgesetz der Gase: Gay-Lussac, Dalton, Dulong und Petit, Rudberg, Magnus, Regnault—*M.* 3.00.

No. 45. Elektrochemische Untersuchungen: Davy—*M* 1.20.

No. 52. Die Kräfte der Elektrizität bei der Muskelbewegung: Galvani—*M.* 1.40.

No. 58. Chemische Abhandlung von der Luft und dem Feuer: Carl Wilhelm Scheele—*M.* 1.80.

These convenient little volumes are issued in a neat, flexible binding, and at prices which are designed to bring them within the reach of everyone. J. E. T.

[1] This Journal, 16, 157.

NOTE.

HELIUM.

The announcement made several months ago[1] of the discovery in the mineral "clèveite" of the gas which produces the line D_3 in the spectrum of the solar chromosphere, naturally excited widespread interest. The following data have been abstracted from a paper[2] read by Prof. Ramsay before the (London) Chemical Society, and will give some idea of the present state of the work of investigation.

Palmieri[3] states that a lava-like substance ejected from Vesuvius, gave a spectrum showing the line D_3; he made no further examination of the substance to prove the identity of its constituent with solar helium. Hillebrand[4] examined a number of uraninites from which gas was evolved; this gas he took to be nitrogen simply, whereas that element was present to the extent of only about 10 per cent.—a quantity sufficient, however, to mask many of the characteristic properties of helium. In the search for substances which would combine with argon, Ramsay was led to examine the gases given off on heating clèveite and certain related minerals, and has been able to prove that they consist, in great part, of helium.

About thirty minerals were examined; of these about half gave gas-mixtures in which the quantity of helium ranged from a mere trace to the point where it was practically the sole constituent. Many of these minerals contain uranium as an essential constituent—one, pitchblende, being practically pure uranium oxide,—but by no means all: yttrium and thorium are frequently constituents of minerals yielding helium under the influence of heat. The manner in which the gas is held by the mineral is unknown. Experiments in which uranium oxide was heated in contact with helium, or uranium itself in a mixture of helium and oxygen, and the apparatus allowed to cool, gave only negative results: helium was not absorbed. Similar experiments are still to be made with the oxides of thorium and yttrium, and with a mixture of these with uranium oxide.

The helium evolved from these minerals was frequently mixed with hydrogen; this was removed with the aid of hot copper oxide, or of metallic palladium—the latter reagent being used in certain cases to decide the question whether the

[1] W. Ramsay: Proc. Roy. Soc., **58**, 65; etc.
[2] Ramsay, Collie and Travers: Proc. Chem. Soc., 1895, 684.
[3] Rend. Acc. Napoli, **20**, 233.
[4] Bull. U. S. Geol. Survey, **78**, 43.

hydrogen was or was not in combination. Nitrogen was also a usual constituent; it was removed, as in the case of the purification of argon, with hot magnesium, or by sparking with an excess of oxygen over a solution of caustic soda, the oxygen residue being afterwards removed with the aid of potassium pyrogallate. The densities of the several specimens of the gas, obtained from different sources or by different methods, averaged 2.18, the density of hydrogen being taken as the unit; after being mixed and submitted to further processes of purification, the density, determined with the aid of a larger bulb, was found to be 2.218. After circulation over hot magnesium and copper oxide the density was finally reduced to 2.133. Determinations of the wave-length of sound in the purified gas gave, as the ratio between the specific heats, the figure 1.632 and, finally, with the gas whose density had been found to be 2.133, the figure 1.652, the theoretical figure for a monatomic gas being 1.66.

"In the case of argon the purest specimen obtained gave for the ratio 1.659; and, as remarked,[1] not much dependence can be placed on the accuracy of the last figure.

"The result of these experiments goes to prove that the density of the gas named helium is not less than 2.13, and that it has the same claim to be considered a monatomic gas as mercury gas; or if it is a mixture, it must be a mixture of monatomic gases."[2]

One volume of water was found to be capable of dissolving only 0.0073 volume of helium, the lowest coefficient on record. Alcohol and benzene do not dissolve the gas at all. Prof. Olszewski is at present engaged in experiments to determine the critical constants of pure helium. The refraction-coefficient has been determined by Lord Rayleigh.

The study of the spectrum of helium by Mr. Crookes, has led to some very interesting results, a notable one being, that "at least two of the lines in the spectrum of helium, seen with a wide-dispersion prism, are coincident with two of the argon lines. These occur in the red, and comprise one of each of the two pairs of characteristic argon lines. This observation has been frequently repeated, using for the purpose spectroscopes of different dispersive power, and throwing into the field both spectra at the same time, with an exceedingly narrow slit; and we may say that if not absolutely identical, the lines are so near that it is not possible, with the means at our disposal, to recognize any difference in position. But the relative brilliancy is by no means the same. One of the argon lines, rather faint, is coincident with the prominent red of the

[1] Phil. Trans., 1895, 52.

[2] Ramsay, Collie and Travers: *Loc. cit.*, 696.

helium spectrum, and one of the strong red argon lines is coincident with a faint red line in the helium spectrum.''[1]

In concluding this paper the authors say: ''It cannot be doubted that a close analogy exists between argon and helium. Both resist sparking with oxygen in presence of caustic soda; both are unattacked by red-hot magnesium; and, if we draw the usual inference from the ratio between their specific heats at constant volume and at constant pressure, both are monatomic gases. These properties undoubtedly place them in the same chemical class, and differentiate them from all known elements.''[2]

''How does argon happen to occur in the air and helium only in minerals? Why is helium not present in air?

''A satisfactory answer to this question is, we think, contained in a paper by Dr. Johnstone Stoney.[3] He there shows that were hydrogen to be present in air (and it might be present, in spite of the oxygen with which it would be mixed, for a small quantity would surely escape combination), it would, in virtue of the velocity of its own proper molecular motion, remove itself from our planet, and emigrate to a celestial body possessing sufficient gravitational attraction to hold it fast. Dr. Stoney suggests this explanation to account for the absence of an atmosphere and of water-vapor on the moon, and for the presence of an atmosphere of hydrogen on the sun. It would also account for the absence of helium in our atmosphere, and for the presence of the chromopheric line D_3. Of course if an element can form compounds, or if it is absorbed by solids, as helium appears to be, it will, like hydrogen and helium, be found on the earth.''[4]

Finally, the authors suggest, as the only explanation of the facts known to them, that argon and helium are both mixtures, and that they contain a common constituent. Experiments having for their end the determination of this question, are already in progress.

W. W. R.

[1] Ramsay, Collie and Travers: *Loc. cit.*, 1895, 698.
[2] *Ibid*, 699.
[3] Chem. News, 71, 67.
[4] R., C., and T.: *Loc. cit.*, 700.